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FINAL REPORT

ON

HYDROTHERMAL GROWTH OF LARGE RUBY SINGLE CRYSTALS
PHASE I

Roch R. Monchamp, Richard C. Puttbach, J. W. Nielsen

FOREWORD

This Final Technical Report covers all work performed under Contract AF 33(657)-10508 from 1 January 1963 to 15 April 1965. The manuscript was released by the author in October, 1965, for publication as an AFML Technical Report

This Contract with Airtron, a division of Litton Industries, Morris Plains, New Jersey, was initiated under Manufacturing Methods Project 8-132, "The Hydrothermal Growth of Large Ruby Crystals". It was accomplished under the technical direction of Mr. Robert C. Bratt of the Electronics Branch (MATE), Manufacturing Technology Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

Closely related efforts are covered under MMP No. 7-988, "The Growth of Zinc Oxide Crystals"

Dr. Roch R. Monchamp, Manager, Crystal Growth Research and Development, of Airtron's Solid State Laboratory, was the Project Director. Others who co-operated in the research and in the preparation of the report were Dr. J W. Nielsen, Manager, Solid State Laboratory; Richard C. Puttbach, Project Engineer; and Peter Wegesser, Laboratory Technician. This report has been given Airtron's report number R11-493.

This project has been accomplished as a part of the Air Force Manufacturing Methods Program, the primary objective of which is to develop, on a timely basis, manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas.

> Design of a pilot line for ruby crystal growth, hydrothermal growth of ruby crystals, growth of sapphire crystals, ruby solubility and sapphire solubility.

Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.

MELVIN E FIELDS, Colonel, USAF
Chief, Manufacturing Technology Division
Air Force Materials Laboratory

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ABSTRACT

The hydrothermal growth of ruby crystals has been taken from the point of feasibility to the point where techniques, process and equipment have been developed whereby large crystals have been grown from which laser rods were cut.

The development of this process involved a study of the solubility of Al_2O_3 in K_2CO_3 as a function of pressure (5,000 - 30,000 psi), temperature (400°C - 600°C) and mineralizer content (2 - 7 m). The solubility was determined by the sample weight loss technique in a hydrothermal research apparatus. It was found that the solubility of Al_2O_3, in the ranges studied, increased with increasing molality and temperature but that the solubility was essentially independent of pressure. Solubilities of 2 - 9 weight percent of Al_2O_3 were observed under the preceding conditions. Using these data as a guide, the parameters affecting growth rate were studied while carrying out investigations to improve quality. The growth rate increased as expected with temperature and solvent concentration but exhibited a very rapid increase with pressure at about 15,000 psi. This was due to what appears to be a transition from a two-phase fluid below 15,000 psi to a single-phase fluid above this pressure.

Growth of high quality crystals was found to be dependent upon seed source, seed orientation and warm-up procedure. It was found that the highest quality growth was obtained when molten salt plates were used as seeds. These plates have $\{0001\}$ faces as major faces for crystal growth. The warm-up of a vessel was found to be critical and a cycle was evolved which had a rapid warm-up to avoid complete dissolution of the seeds followed by a slow introduction to growth conditions. The conditions established for the growth of good quality crystals at reasonable rates are as follows: 6 m K_2CO_3 as solvent, 25,000 psi, crystallization temperature 525°C and nutrient temperature 530°C. The problem of banding appeared to be dependent on K_2CO_3 content of the solvent and the severity of this banding decreased as the K_2CO_3 molality increased. Veiling or cracking was reduced by using the molten salt seed plates and modified warm-up procedure.

From crystals grown by these procedures and with these conditions, several rods were fabricated into laser rods which, when pumped with a flashlamp, were caused to lase. This lasing action was about the same threshold and output as flame fusion ruby but was peculiar in that no spiking in the output was observed

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1.0 INTRODUCTION

The four methods of synthesizing ruby crystals are flame fusion, molten salt, hydrothermal and, most recently developed, Czochralski. For many years, the flame fusion, or Verneuil, technique has been used to yield gem stones and industrial quality ruby. However, with the development of the ruby, solid state lasers for high power application, it has become important to develop a technique other than flame fusion. The problem with flame fusion crystals is their low quality due to strain induced by steep temperature gradients involved in growing these crystals.

At the time this work began, the following statements were true concerning the remaining techniques. The molten salt method is not practical because of the size limitations of crystals. The Czochralski technique has recently been used successfully to obtain crystals of ruby. This process is expensive because it requires almost constant attendance of technical personnel, expensive crucibles and expensive furnaces. Of the four processes ultimately capable of yielding high quality, large crystals in large quantities, the hydrothermal process appears to be the most economical. Now, both the importance and relative position of each process is even more evident; flame fusion crystals, though improved, are usually strained; Czochralski crystals are better quality but very expensive; and feasibility for growing high quality, cheap ruby hydrothermally has been demonstrated.

Normally, crystal growth from aqueous solution is carried out at atmospheric pressure and temperatures close to room temperature. The hydrothermal technique is one which allows crystallization to be carried out under a wide range of temperatures and pressures. The higher pressures and temperatures employed in this method provide a means of obtaining solubilities and nucleating conditions for crystals which would be difficult to grow using other techniques.

In operation, an aqueous solution is held at a high temperature and pressure in order to dissolve the source material (nutrient) in one part of the system, transport the dissolved nutrient to another part of the system and deposit it onto a seed crystal epitaxially. The process is carried out in vertically mounted, sealed autoclaves along which a temperature difference (ΔT) is imposed between the top and bottom. The nutrient is usually placed in the bottom, hotter portion of the autoclave chamber while the properly oriented single crystal seeds are suspended in the upper, cooler region as in Figure 1.

The aqueous solvent in the region of the nutrient becomes saturated with nutrient which is then transported by thermal convection to the cooler portion of the autoclave. In this region, the solution is supersaturated with respect to the seed crystals and, therefore, deposits the solute on the seeds. The now cooler and depleted solvent returns to the nutrient region by convection where, not now being saturated, it may again dissolve the nutrient material. Obviously, the process is continuous and stops only when the nutrient supply is exhausted.

- 1 -
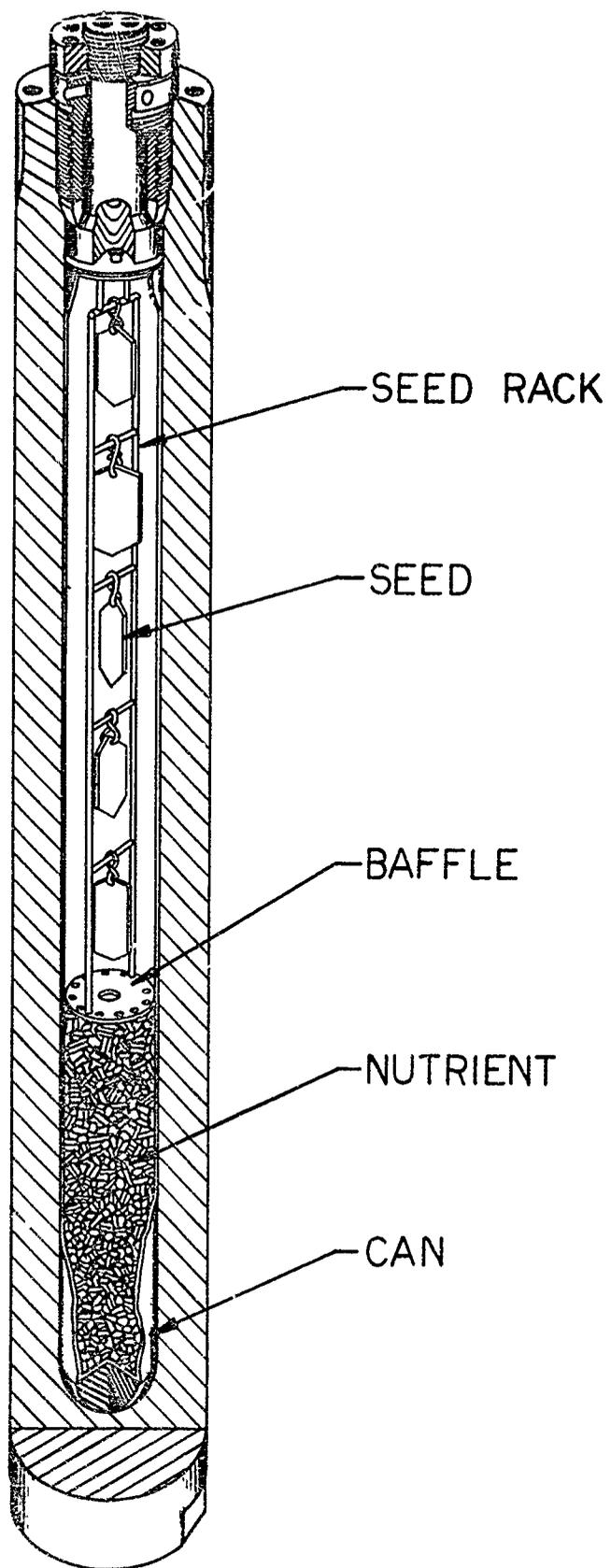
Figure 1 - Hydrothermal System

- 2 -

Introduction (continued)

More detailed descriptions of the hydrothermal process and equipment can be found in review articles by Laudise and Nielsen,[1] and Laudise [2] These articles, particularly that of Laudise and Nielsen, also emphasize the hydrothermal process for quartz work.

Three years ago, hydrothermally prepared ruby was a laboratory curio Laudise and Ballman[3] at Bell Telephone Laboratories had prepared some crystals of ruby by doping sapphire with $K_2Cr_2O_7$. These crystals were relatively small and of very poor quality. Nonetheless, Laudise had demonstrated the feasibility of crystallizing chromium doped alumina. Laudise and Ballman performed some phase stability experiments in the system $Al_2O_3-H_2O-Na_2CO_3$ confirming the results of Ervin and Osborn.[4] Barns, Laudise and Shields[5] also studied the solubility of sapphire in Na_2CO_3 and did some crystal growth experiments. The extent of this work can be obtained from References 1 and 2. White[6] of General Electric, Wembley, had done some solubility studies but discontinued his work because of low rates and low quality obtained in his system. Although less is known of White's work, it appears that he obtained growth only when he used carbonates of the lower members of the alkaline metal series. Russian workers have also been active in the field and have published at least one article on the hydrothermal growth of ruby.[7] In their article, they reported neither high rates nor high quality.

With these data at hand, a program to investigate the growth of ruby hydrothermally was begun. This program had as its goal the development of a manufacturing process, techniques and equipment for the hydrothermal preparation of large, high quality ruby crystals. The size set for such rubies at the time the Contract was let was 20 grams and the quality was to be such that rods could be fabricated from these crystals in order to test them for laser action.

2.0 PILOT LINE

2.1 Laboratory Facility

A pilot line for the hydrothermal growth of large ruby crystals was designed and assembled. A 20-feet long x 4-feet wide x 4-feet deep pit with reinforced concrete walls was constructed in the laboratory to contain the autoclaves and furnaces when in operation. This pit provides personnel protection against scalding or fragmentation which could result from equipment malfunction. The pit contains six furnaces, four large ones for the large A-286 autoclaves and two for the small Waspalloy vessels, and a saturable core reactor for each furnace. At one end of the pit is located a sump and automatic pump in the event of ground water seepage into the pit. This sump area of the pit is also used for cleaning and cooling of the autoclaves. This equipment was obtained under Air Force Facilities Contract AF 33(657)-12307.

The furnace heights are adjusted so that the tops of the autoclaves are just floor level. The pit area is covered by removable steel grill sections. Mounted on the nearest wall are the temperature controllers and programmers for the hydrothermal furnaces. A one-thousand pound capacity travelling hoist is mounted overhead so that the autoclaves may be readily moved.

The laboratory is also provided with chemical work benches for silver can preparation, loading and storage. A fume hood and large overhead exhaust fan supply ventilation for protection against chemical vapors.

A floor plan of the laboratory showing its hydrothermal and molten salt facility is shown in Figure 2. Figure 3 is a photograph of the pit area showing the larger furnaces and autoclaves.

2.2 Standard Equipment

2.2.1 Tem-Pres Research Unit

A Tem-Pres apparatus, Figure 4, with four stations was used to carry out the solubility and initial crystal growth experiments. Each station consists of a furnace with temperature control equipment, an autoclave (stellite, 3/8 inch i.d. x 7 inches i.l.), and a pressure gauge. A hydraulic water pump is also attached to this apparatus to both generate and regulate the pressure of any particular station by a system of high pressure tubing and valves.

2.2.2 Hydrothermal Crystal Growth Autoclaves

In order to grow crystals weighing 20 grams or more as specified in the Contract, it was necessary to purchase vessels of sufficient cavity size to contain such crystals. The cavity size was 1.5" x 15", large enough so that crystals at least one inch in width could be grown in suitable silver cans.

- 4 -
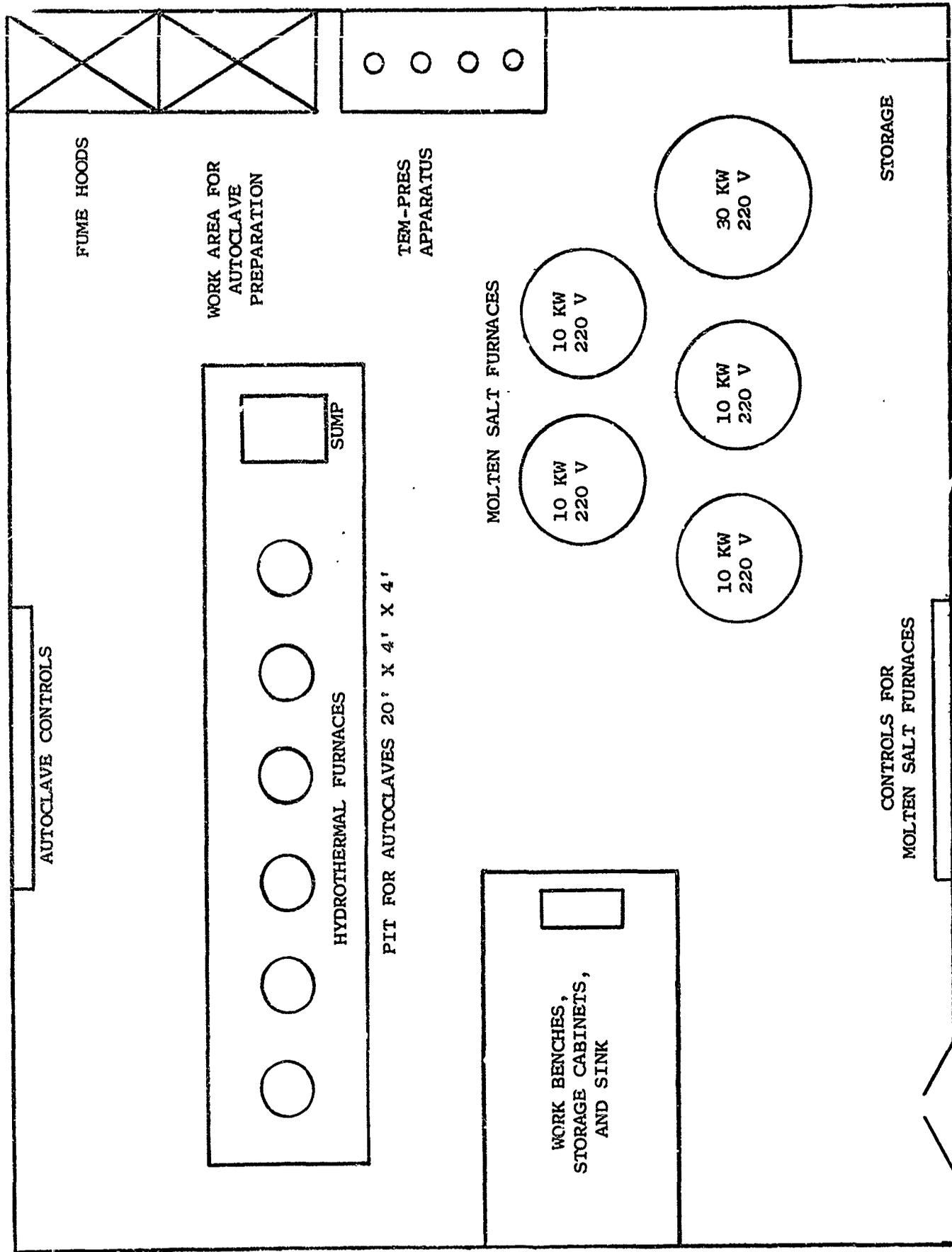
Figure 2 - Floor Plan - Hydrothermal Laboratory
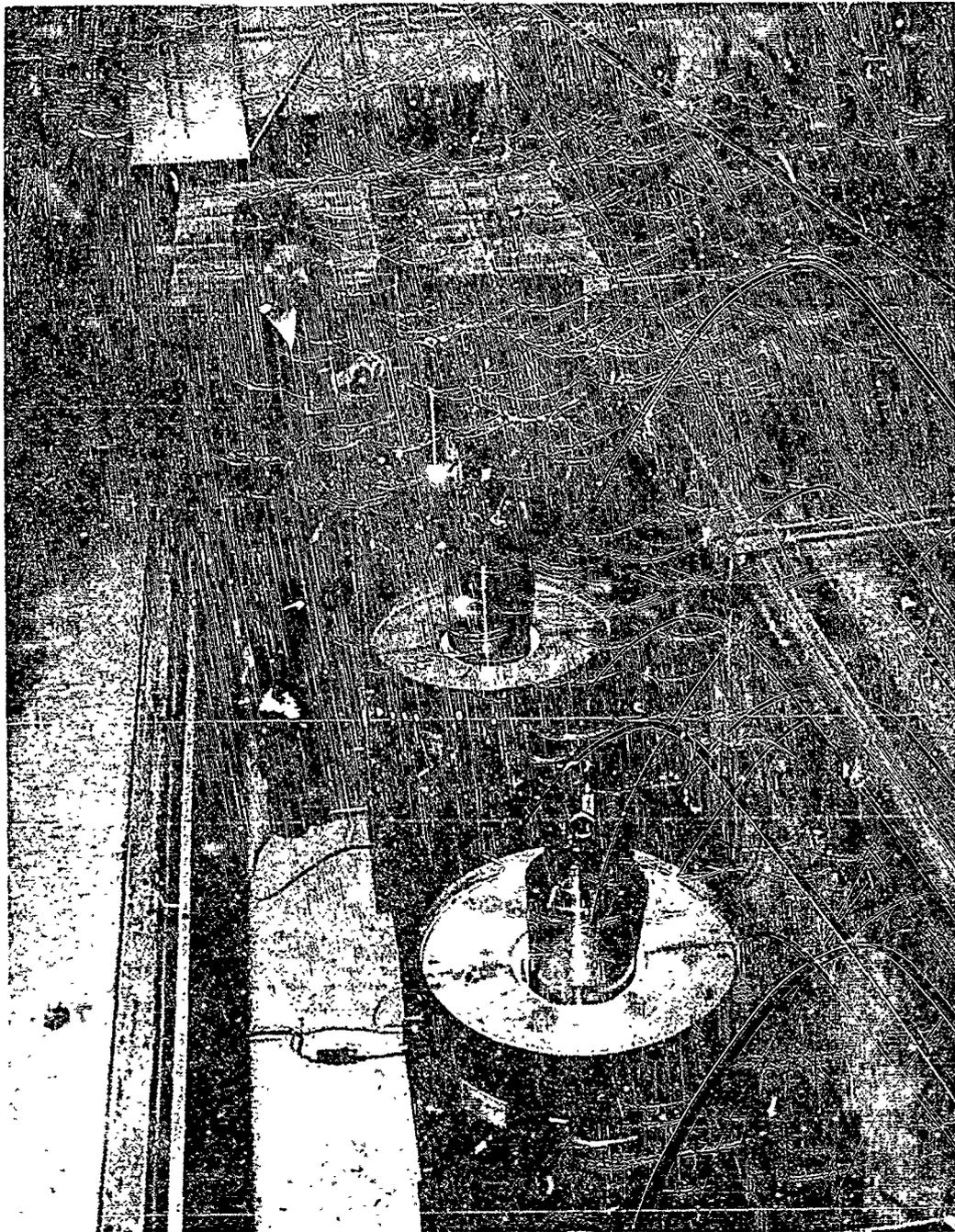
Figure 3 - Pit Area, Furnaces and Autoclaves
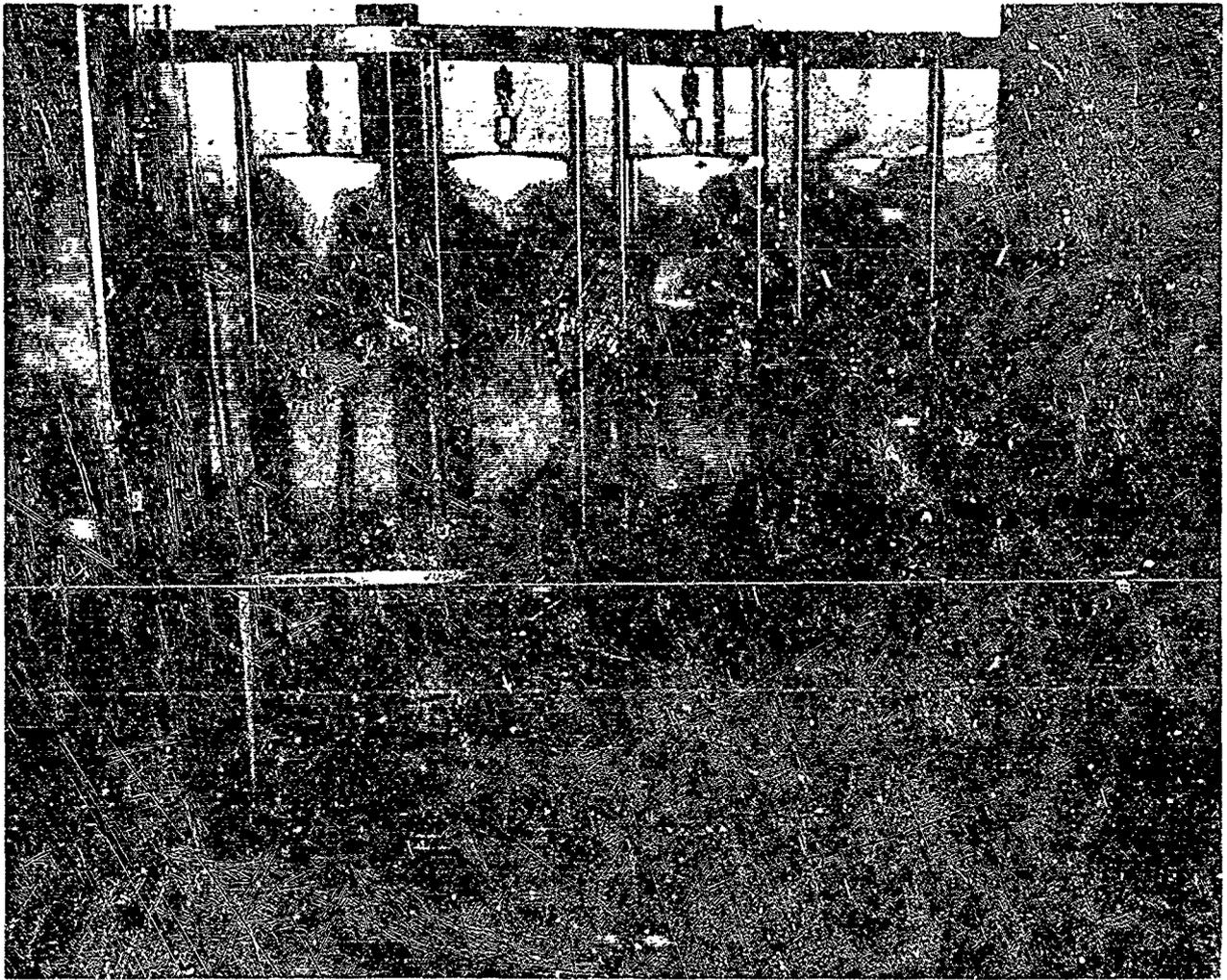
Figure 4 - Airtron's Tem-Pres Apparatus

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Pilot Line (Continued)

Of the available materials for autoclave construction,
that of maximum pressure and temperature (P-T) limits was chosen since,
at the time of purchase, these variables for crystal growth were not
known. It was also necessary to select a seal design capable of con-
taining the high pressure-temperature conditions. As a result of these
criteria, the vessel as shown in Figure 5 was chosen, - the material of
construction being Waspalloy whose pressure-temperature ratings are
40,000 psi and 650°C for 10,000-hour life.

Another size autoclave, Figure 6, was also available
under Contract AF 33(657)-8795 for larger runs. These vessels were con-
structed of A-286 and, therefore, limited to 590°C and 30,000 psi. In
such vessels, 2.5 inch wide crystals could be grown.

The autoclaves were manufactured by Autoclave Engineers,
Inc., Erie, Pennsylvania, who had developed what is called a "modified
Bridgman" seal. This seal is that used by Western Electric for their
quartz manufacture and believed to be the best workable, high tempera-
ture, high pressure seal. This seal is described as "self-energizing"
since it relies upon the internal pressure developed by the fluid under
growth conditions to provide for sealing force. The vessel is initially
sealed by the main nut's downward thrust on the seal ring and then up-
ward thrust on the piston by means of the set screws in the lock nut.
Opposite screws are tightened in turn by means of a torque wrench to
10 ft. lbs. each. This sealing initially causes the seal ring to make
line contacts with the autoclave body and plunger. As the internal pres-
sure develops, the plunger is thrust upward causing the seal ring to de-
form elastically and produce surface contacts. This self-energized seal
provides better sealing as the internal pressure increases.

Several difficulties with this seal were encountered
during this development program and are discussed in later sections.
One, however, is noted here since it involved an unpredicted behavior
of the seal. While this seal ring does deform elastically at lower
pressures and temperatures, it was found that plastic deformation oc-
curred at higher temperatures and pressures (500°C and 20,000 psi) which
were still well below the maximum temperature and pressure for which the
vessels were rated. This deformation does not interfere with the vessel
closure but does necessitate machining the seal ring after each use and
careful preparation of all sealing surfaces prior to use.

2.2.3 Silver Liner or Cans

Noble metal containers or cans are used in order to
prevent contact of the autoclave body with the basic solutions used in
ruby and sapphire crystal growth. This is necessary since the solutions
would corrosively attack the autoclave metals under hydrothermal condi-
tions. The containers were made of seamless, fine silver tubing and
flat circles of the same material. The baffle and seed rack were also
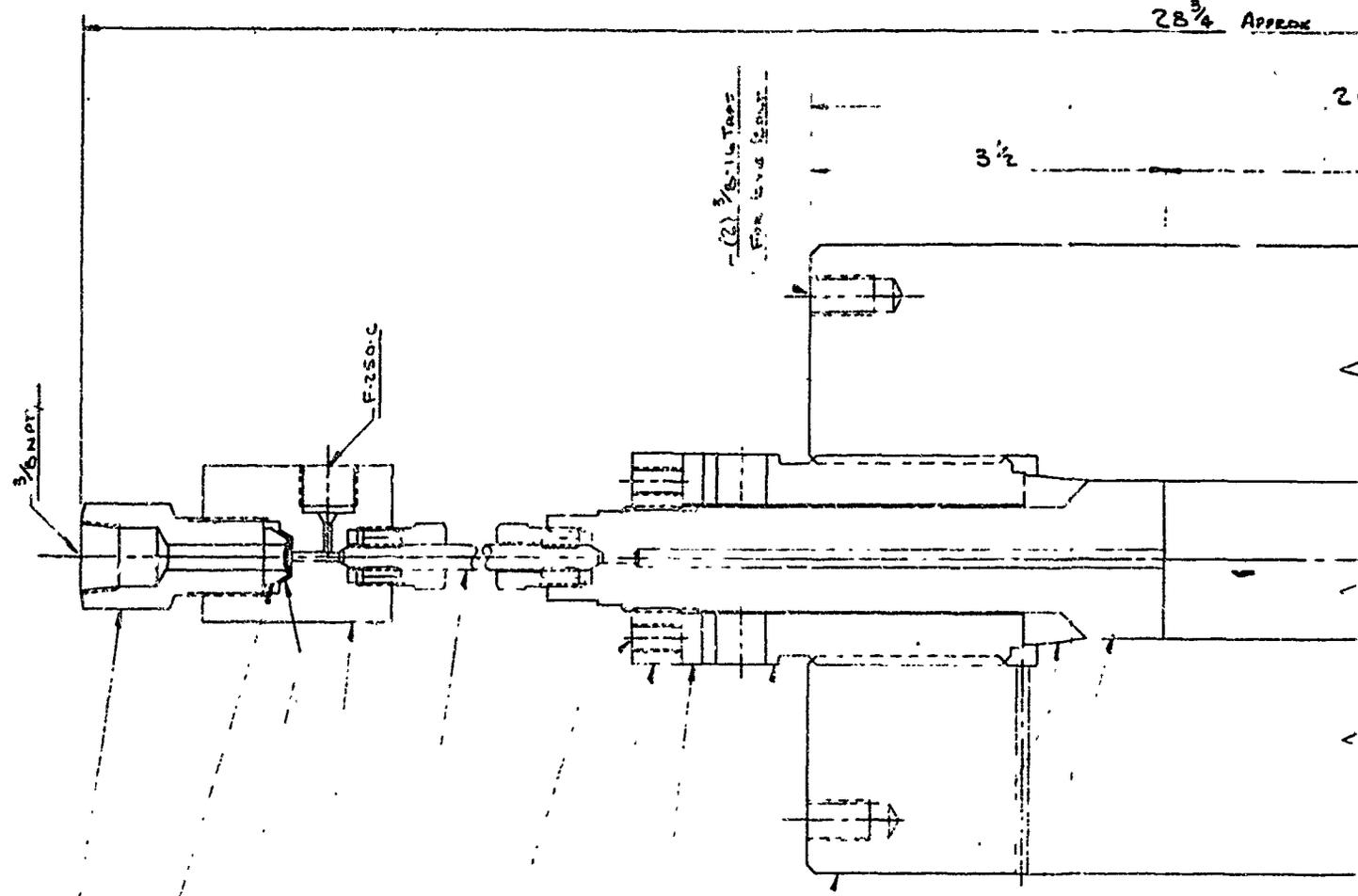
- 8 -

28¾ APPROX

.21

3½

~(2) ⅜-16 TAPS FOR EYE BOLT

F-250-C

⅜ NPT

HOLD DOWN NUT - 416SS
DWG 10-241-2

HOLD DOWN RING - TEFLON
DWG 10-742-2

¼ RUPTURE DISC - INCONEL
RATED 60,000 PSI @ 72°F

SAFETY HD BODY - 316SS
DWG 10-755-2

NIPPLE ¼ OD x .085 ID
316SS PART 301-4402

(6) ¼-20 SET SCREWS
MAT'L A286 PART 100-1218(IN)

LOCKNUT - 1625-G
DWG 20-6290 ITEM 3

THRUST WASHER-1625G
DWG 20-6290 ITEM 2

MAIN NUT - WASPALOY
DWG 20-6290 ITEM 1

BODY - WASPALOY
DWG 20-6289

SEAL RING WASPALOY
DWG 20-6290 ITEM 2

GOUGE - WASPALOY
DWG 10-6290 ITEM 4

WORKING PRE

HYDRO TEST F

1

28¾ Approx

21¼

3½ 15" 1"

(2) ³/₈-16 Tap.
For Eye Bolt.

1½ D.

5½ Across Flats.

9 Dia.

Dwg. 20-6990 Item 2
Main Nut - Waspaloy.
Dwg. 20-6990 Item 'L'

Body - Waspaloy
Dwg. 20-6989

Seal Ring Waspaloy
Dwg. 20-6990 Item '2'

Gland - Waspaloy
Dwg. 20-6990 Item '4'

WORKING PRESSURE
{ 40,000 Psi @ 1,300°F. (Designed For 1000 Hg Lines)
34,000 Psi @ 1,300°F. (Designed For 10,000 Hg L 72)
40,000 Psi @ 1,200°F. (Designed For 10,000 Hg Line) }

HYDRO TEST PRESSURE — 60,000 Psi.

Torque Req'd. Per Set Screw To Affect Seal = 2 Ft. Lbs.
Max Recomm. Torque Per Set Screw - 4 Ft. Lbs.

REVISIONS	AUTOCLAVE ENGINEERS, INC.
	ERIE. PENNSYLVANIA
	REACTOR ASSEMBLY
	1½ ID x 15" Length

ORDER	DR. R 1-1-63	DRAWING
AJ-2133	CH.	30-1980
	APP. 1-3-63	

BODY ~ ITEM #1

BREAK THRD SHARP CORNERS .008-45° MAX.

$42\frac{3}{4} \pm \frac{1}{32}$

$41\frac{1}{4} \pm \frac{1}{32}$

$2\frac{7}{8}$

$\frac{1}{8}$ DRILL

15°

1"

$\frac{1}{4}$ R

$\frac{3}{8}$-16 TAP-2 HOLES 180° APART ON 5 B.C.

3.370 ±.010 BORE FULL ACME-4 T.P.I. PER DWG #10E-1143

$5\frac{11}{16}$ DIA

$\frac{1}{8}$ R.

$3^{+.010}_{-.000}$ DIA

6" DIA

$\frac{3}{4}$ FULL THRD

$\frac{15}{16}$

$2\frac{1}{2}$

$3\frac{1}{16}$

$\frac{5}{8} \pm \frac{1}{32}$

$1\frac{1}{2}$

LOCK NUT ~ ITEM #6

$\frac{7}{8}$

$3\frac{3}{4}$ DIA

2"-8 N-2 THRD

$\frac{3}{8}$-11 TAP-8 HOLES 45° APART ON $2\frac{7}{8}$ B.C.

THRUST WASHER ~ ITEM #5

$\frac{3}{16}$

$3\frac{3}{4}$ DIA

$2\frac{1}{32}$ DIA

MAIN NUT ~ ITEM #4

$\frac{3}{8}$

$\frac{33}{64}$ DRILL-4 HOLES 90° APART

$\frac{1}{16}$ R

$\frac{1}{16}$ R.

$3\frac{3}{4}$ DIA

$2\frac{1}{32}$ DIA

$3\frac{1}{4}$ DIA

$3.598^{+.010}_{-.000}$ DIA FULL ACME-4 T.P.I.

$\frac{5}{16}$

BREAK CORNER

$\frac{3}{8}$

$2\frac{13}{16}$

$3\frac{5}{16}$

BREAK ALL SHARP CORNERS
CHAM. THRD 45° TO ROOT DIA.
FRACTIONAL DIM $\pm\frac{1}{64}$
$\sqrt{?}$ FINISH ALL OVER ⎰ EXCEPT AS NOTED
ANGLES $\pm 2°$

1

$42\frac{3}{4} \pm \frac{1}{32}$

$41\frac{1}{4} \pm \frac{1}{32}$

15°

1"

$\frac{1}{16} \times 45°$ BOTH ENDS

$\frac{1}{4}$ R

$5\frac{1}{2}$ ACROSS FLATS

$5\frac{7}{16}$ DIA.

$3\frac{1}{2}$ DIA.

$1\frac{1}{2}$

BODY ~ ITEM #1

⚠ NOTE - THESE DIM'S ADDED TO ONE BODY IN REG # AH 5131
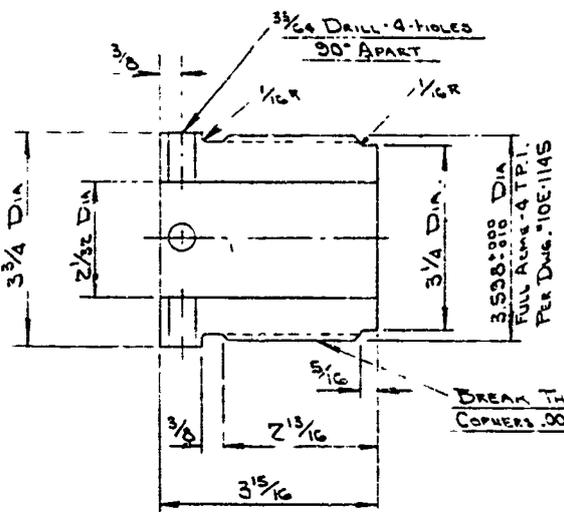
2"-8 $1\frac{1}{2}$ THRD

F-250-C

1" DR.

$\frac{1}{4}$ FULL THRD

$6\frac{3}{16}$

$1.990 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA.

$1.995 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA.

7

45°

2

$2.990 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA.

$\frac{1}{4}$ DRILL

COVER ~ ITEM #2

$\frac{3}{64}$ DRILL - 4 HOLES 90° APART

$\frac{3}{8}$

$\frac{1}{16}$ R

$\frac{1}{16}$ R

$3\frac{3}{4}$ DIA.

$2\frac{3}{32}$ DIA.

$3\frac{1}{4}$ DIA.

$3.538 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA. FULL ACME - 4 T.P.I. PER DWG. #10E-1145

$\frac{5}{16}$

BREAK THRU SHARP CORNERS .008 × 45° MAX

$\frac{3}{8}$

$2\frac{13}{16}$

$3\frac{15}{16}$

MAIN NUT ~ ITEM #4

$\frac{7}{8}$

$\frac{1}{4}$

46°

$6\frac{1}{32}$

$3.159 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA.

$2 \begin{smallmatrix} +.000 \\ -.000 \end{smallmatrix}$ DIA.

.015/.010 FLAT

SEAL RING ~ ITEM #3

PER DWG. #10E-1145

THRU .008

#5
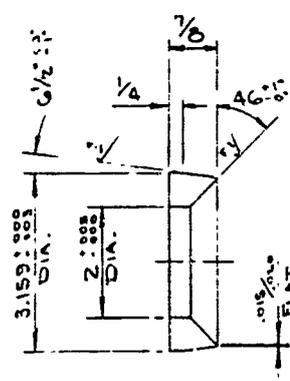
BREAK ALL SHARP CORNERS
CHAM; THED. 45° TO ROOT DIA.
FRACTIONAL DIM ± $\frac{1}{64}$
FINISH ALL OVER } EXCEPT AS NOTED
ANGLES ± 2°

REVISIONS			AUTOCLAVE ENGINEERS, INC.
BODY MACHINING & NOTE ON $5\frac{13}{16}$ DIA ADDED	R.P.	10/11/62	ERIE, PENNSYLVANIA
			REACTOR DETAILS

ORDER	DR. MITCH 8-11-62	DRAWING
AH-5131	CH. O	30-1928-1
	APP.	

2

Pilot Line (Continued)

made of fine silver and the design is shown in Figures 7 and 8. The two baffle designs shown in Figure 9 were used, but that of the circumferentially drilled holes was thought to be best and so became the standard.

Two sizes of cans were used:

1. 1.440 inches o.d. by 14.5 inches long.
2. 2.940 inches o.d. by 35.0 inches long.

2.2.4 Hydrothermal Furnaces

The furnaces used to heat the autoclaves are shown in Figure 10. The furnaces, originally designed and built by Research & Development Products, Inc., New Market, New Jersey, consist of clam shell type of heater sections constructed of Nichrome resistance wire cemented in a grooved ceramic, insulating wool materials and outer metal shells.

Since the bottom section of the autoclave must be the hotter section, it was found that the bottom should receive the greatest power and only slight or auxilliary heating was necessary in order to level out or adjust the proper temperature difference between sections.

After a number of failures in the bottom section, this section was redesigned so that the bottom of the vessel rested on an electric range heater. The main heat was applied to the bottom of the vessel by this electric range element. Better contact and more even heat distribution was achieved by placing an 8" x 8" x 1/2" stainless steel plate over this heater.

It was found that the amount of power for a fixed set of conditions varied somewhat for each combination of autoclave vessel, furnace and controller.

2.2.5 Temperature Control

The power to the electric range surface heating element or hot plate element is controlled by a saturable core reactor through a West Programmer Controller: a control thermocouple is cemented to the firebrick immediately below the hot plate element. The clam shell heater is also controlled by the West instrument by means of a manually set ratio for power distribution to each furnace element. This distribution of power is accomplished by the S-92 option of the West JSBG-3R Program Controller, which allows the output from one temperature controller to drive-up to three saturable reactors. In this case only two reactors are used. A schematic of the control system is shown in Figure 11. The control thermocouple as shown in Figure 10 supplies the input signal for the operation of the controller and driver.
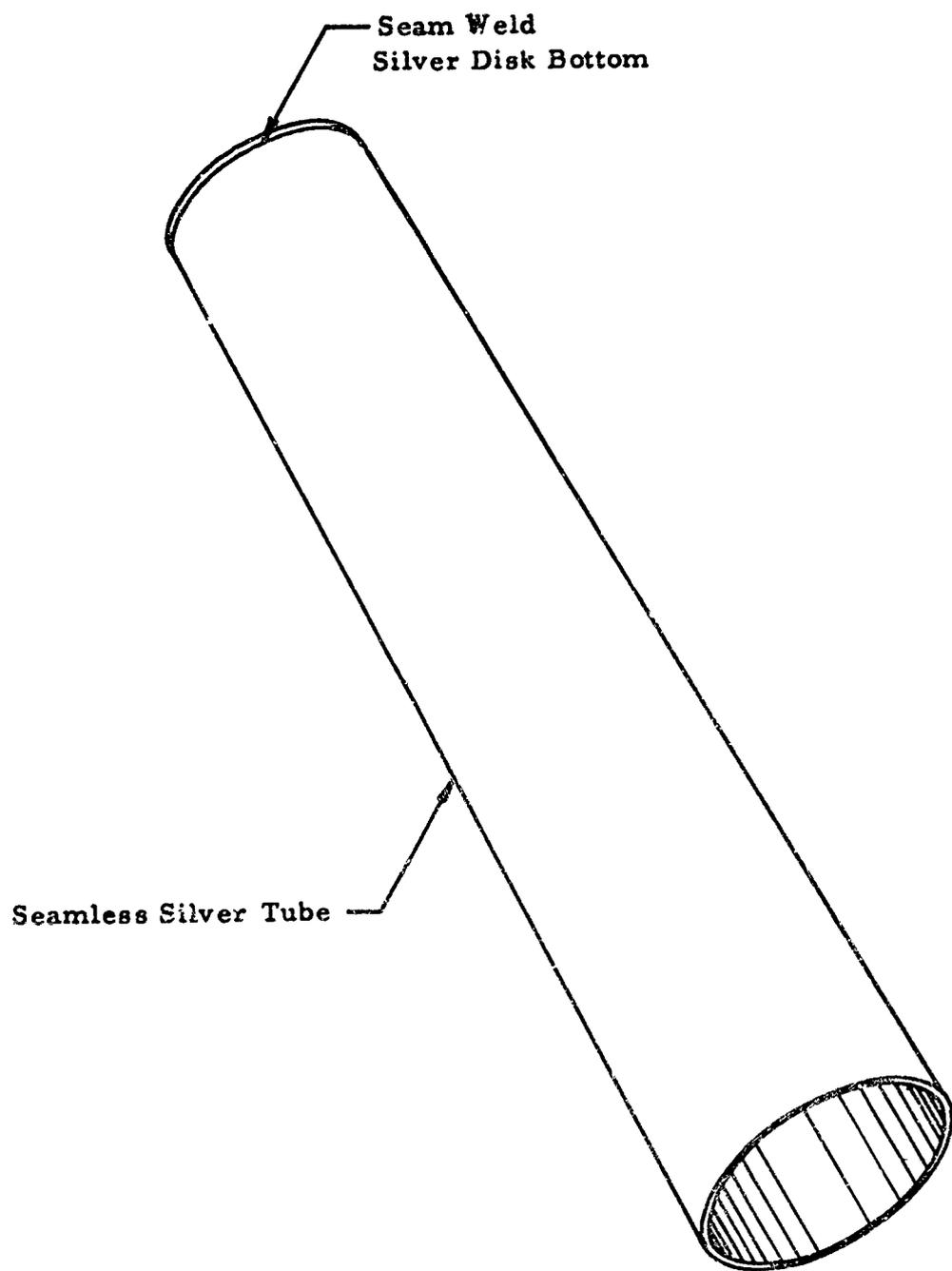
Figure 7 - Silver Can Design

- 12 -
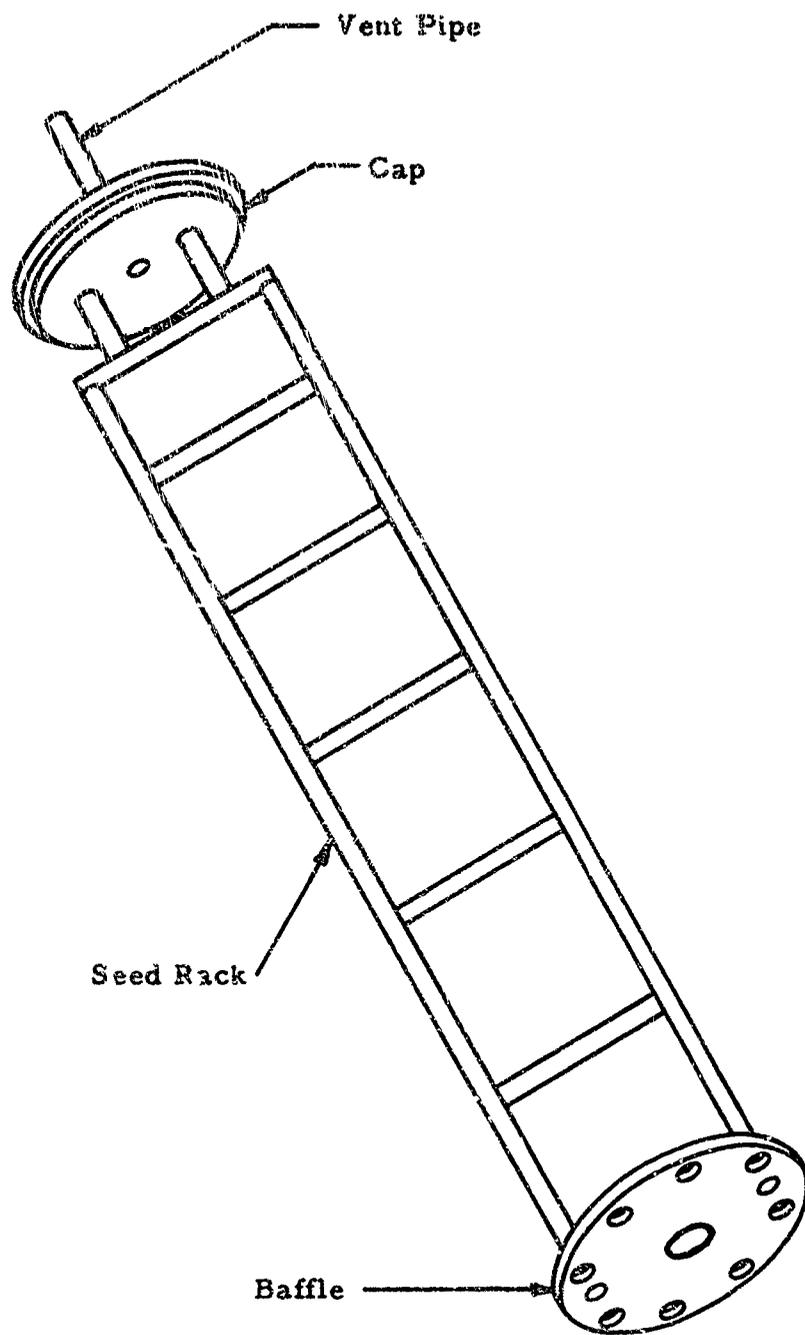
Figure 8 - Seed Rack Design

SCREEN OVER

(a)

(b)

Figure 9 - Baffle Designs

Power Leads to
Reactor R2

Clam Shell Heater —

Stainless Steel Tube

Stainless Steel —
Plate

Electric Range
Heating Element

Control
Thermocouple

Power Leads to
Reactor R1

Firebrick —
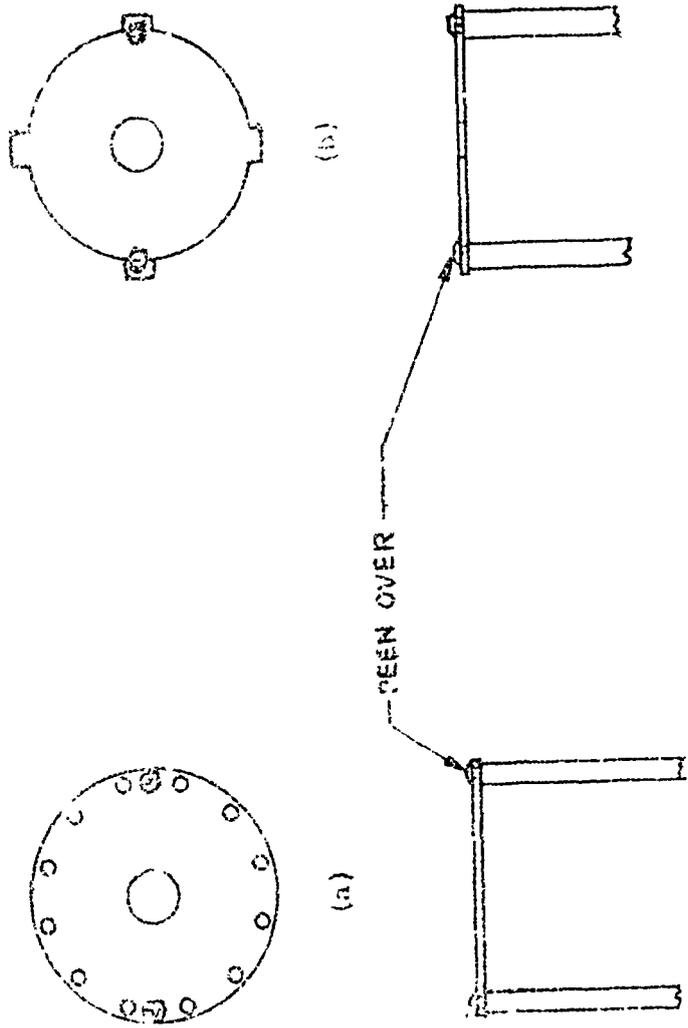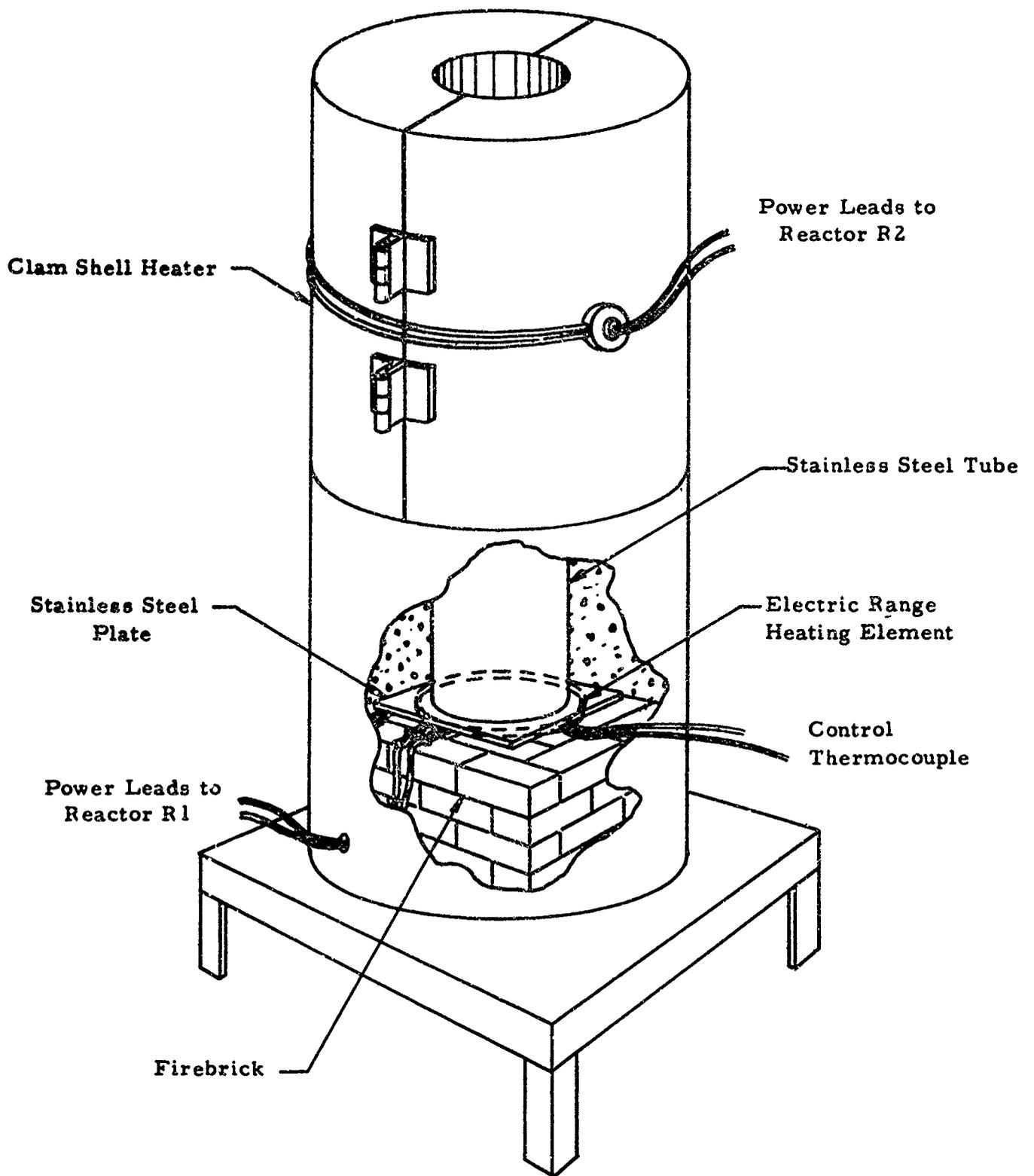
Figure 10 - Hydrothermal Furnace

JSB-3
INSTRUMENT

DRIVER

MANUAL ADJUST TO RAISE
OR LOWER TEMPERATURE
IN ANY ZONE.
CW FOR MAXIMUM POWER
(S-92 FEATURE)

R1, R2, OR R3 REACTORS

ZONE   ZONE   T/C ZONE
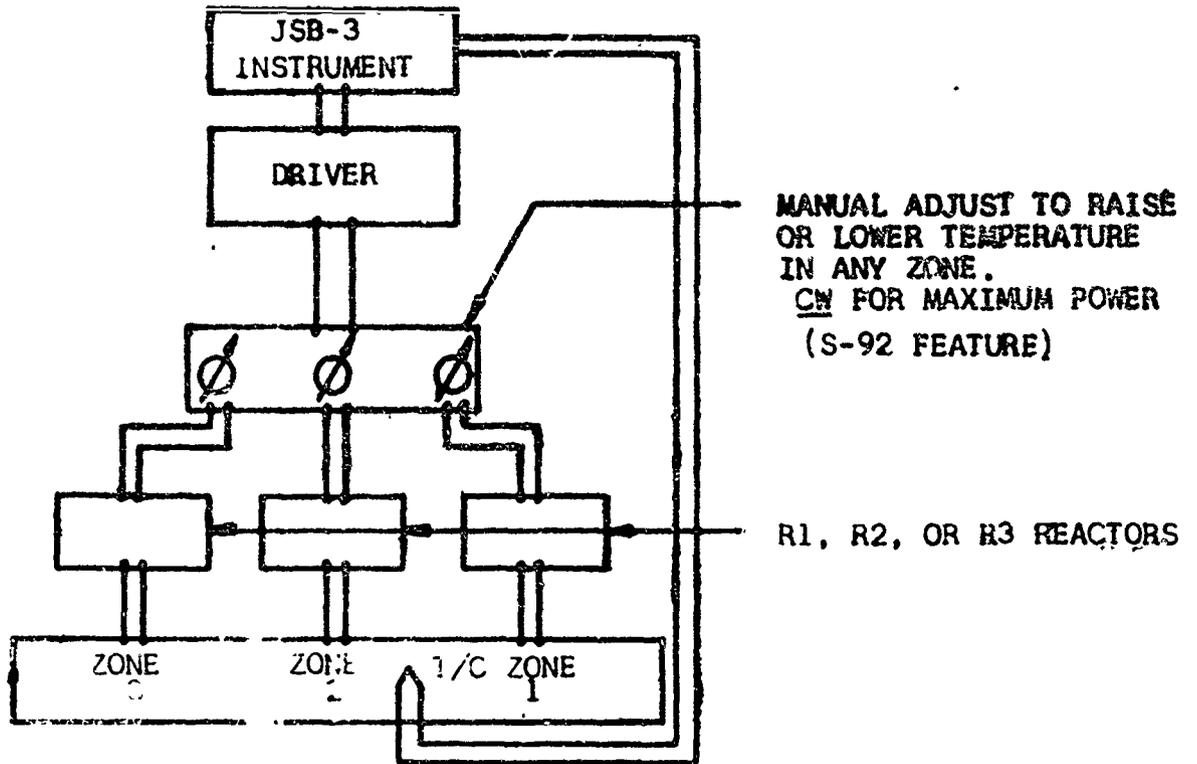
Figure 11 - Schematic of West S-92

WEST Instrument
CORPORATION
Chicago

R11-493

Pilot Line (Continued)

Reactor R1 as shown in Figure 11 is used to power the hot plate while
Reactor R2 is used to power the clam shell heater. The ratio control
of the two heaters allows much greater latitude in temperature profile
adjustment than would be possible with a single heater by varying ther-
mal insulation conditions. Other operating temperatures are obtained
by means of thermocouples attached by metal straps at various positions
along the length of the autoclave. It has been shown elsewhere that
these externally measured temperatures correspond closely to the inter-
nal temperatures. For purposes of convenient reference, an "operating
average temperature" has been defined as the numerical average of these
measured temperatures.

2.2.6 Pressure Measurement

Pressure in the system is obtained by direct reading
of Bourdon type gauges connected directly to the internal cavity of the
autoclave. Since the walls of the silver cans are deformed under only
slight pressure, the gauge pressure is a fairly accurate measure of the
internal pressure of the can. Ashcroft Maxisafe gauges (Autoclave En-
gineers, Inc., authorized vendor) using Monel Bourdon tubes connected
to the autoclaves by F250-C fittings were used.

2.3 Equipment Developed During Contract

Use of the autoclaves and associate equipment required the
development of some additional tools whose necessity had not been anti-
cipated.

2.3.1 Autoclave Opener

Closure is achieved with manual force only, accord-
ing to the technique described in Section 2.2.2. Operation of the auto-
claves proved that the manufacturer's recommended technique and tools
supplied for loosening the main nut after a run were far from adequate.
In order to unscrew the main nut, and in some cases provide the only
possible technique for removing it, a new anvil-type tool was developed
(Figure 12). This tool was constructed so that it could easily be
clamped onto the main nut by means of two bolts. When in place, two
steel pins in the tool fitted into two opposing holes on the side of
the main nut. The pins in these holes allowed for efficient transmis-
sion of the applied torque. For opening the autoclave, this torque
is provided by striking the arms of the anvil openers with ten-pound
hammers. No pressure-temperature or leak condition produced sealing
of the vessel which could not be opened by this tool.

2.3.2 Large Can Technique

At the onset of this Contract, it had been the prac-
tice, when using noble metal cans, to adjust the volume of the can

- 17 -

Figure 12 - Main Nut Opener

Pilot Line (Continued)

(internal volume) to be nearly equal to the remaining autoclave vol-
ume (external volume). The problem of using noble metal cans rests
in the different equations of state for water and hydroxide or car-
bonate solutions. Since the equations are different, water and any
aqueous basic solutions of the same percent fill and at the same tem-
perature would generate different pressures. It has been found for
all of the common hydrothermal solvents that the pressure generated
by a solution is less than that of pure water.

As a result of these differences, an adjustment of
the fills (internal to external) must be made so that at temperatures
the same force is exerted by the base and water. Any grave imbalance
of fill conditions would lead to severe compressive or expansive dam-
age to the can which could lead to development of a leak. Because of
the pressure-temperature behavior of these fluids, there is only one
pressure and temperature condition at which there will be perfect pres-
sure balance for any set of fills. See Figure 13.

The figure is a somewhat exaggerated pressure-tempera-
ture diagram for water and a basic solution capable of exerting the same
pressures at one temperature only. If one follows along the lines as
if the vessels were warming; i.e., the temperature is increased, it will
be noted that below the point (P, T) the external or water pressure is
greater than the internal or base pressure and thus the can is under
compression. At (P, T) the pressures are balanced so that the can is
subjected to neither compressive nor expansive forces. Higher tempera-
tures again cause an imbalance in pressure but now the can must expand.
Even if the equations of state were known, the can would be subject to
compression at the run warm-up and cool-down; however, the fills for
the pressure-temperature balance point might be calculated rather than
arrived at by experimental observation. Two other points are worth not-
ing at this time.

In addition to not knowing the equation of state for
the basic solution, any such equation would not be quite correct since
at operating conditions the solutions contain 5 - 10 percent Al_2O_3, and
so a further perturbation of the equation would be necessary. Second,
the treatment of this subject has been presented as though the systems
were isothermal. For crystal growth, this is certainly not the case and
some averaging of the equations would be necessary to apply the data.

The problems of severely working the silver can and
matching pressures can be greatly alleviated by the use of a can which
nearly fills the autoclave cavity. This technique was developed during
the Contract when it was thought that the cans might sometimes be com-
pletely crushed when under growth conditions.

By using the large can neither of these conditions can
occur as readily. For example, if the internal fill is larger than it
should be by some reasonable value, the can will be under compression

- 19 -
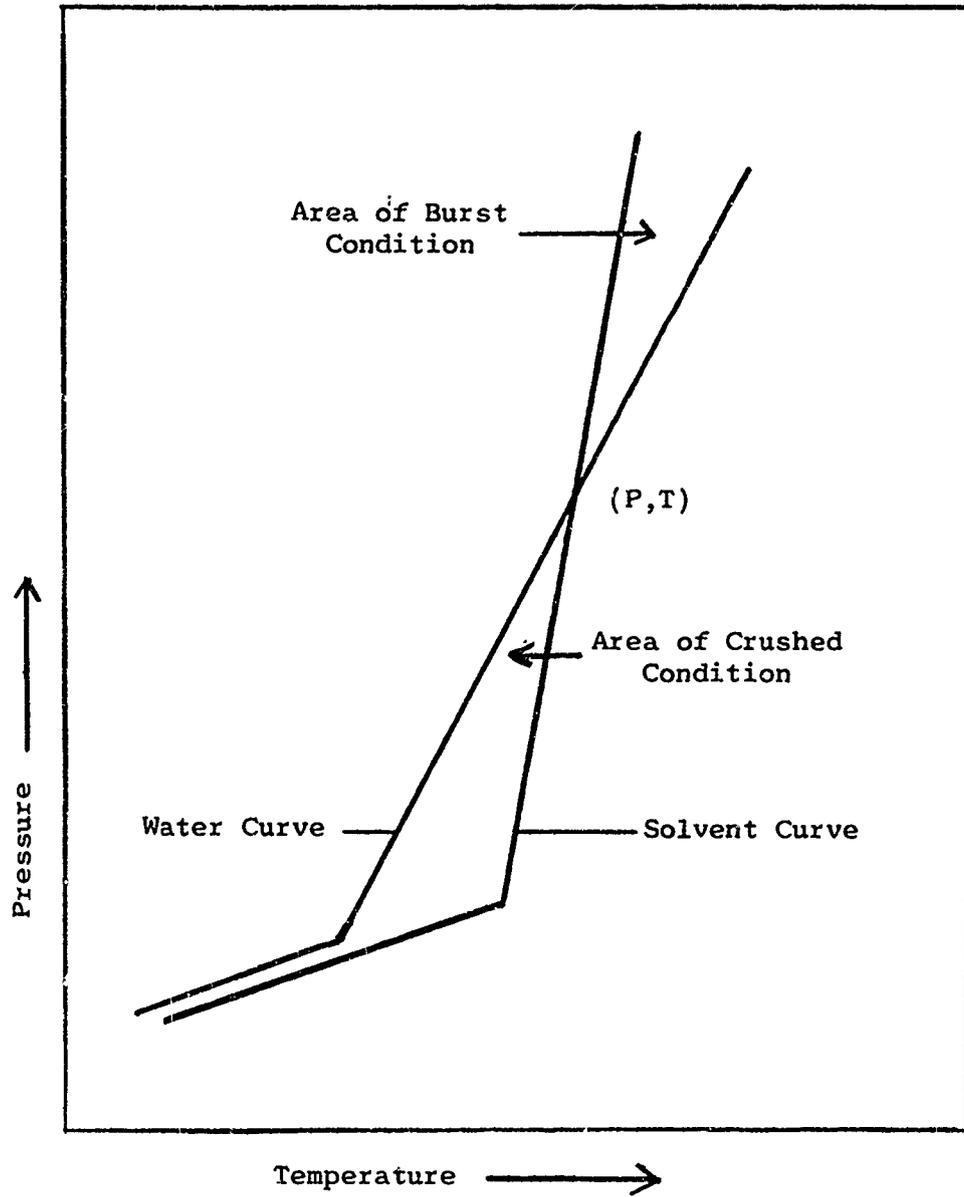
Figure 13 - Schematic for P-T Behavior of Water

Pilot Line (Continued)

during the warm-up. When the crossover point is reached, and the temperature continues to increase, then the can undergoes expansion. Since the void volume is so small now a small percent change of the can's dimensions caused by expansion leads to a large percent decrease in the void volume. The large decrease in void volume also has the effect of producing a correspondingly large increase in pressure of the external volume and hence a restoration force. In other words, a small expansion of the can's dimensions leads to a relatively large decrease in the external volume effectively raising its percent fill. Furthermore, due to the closeness of the fit, bulge cannot occur in any one region and the expansion is spread out over the entire length of the can.

In the case of the internal fill being lower than it should, the can again will be under compression during the warm-up. When the operating temperature conditions are reached, the can is still under compression; however, the effect is now less since the small compression of the can leads to a large increase in the external volume. This increase in external volume essentially leads to a reduction of the fill and reacts to lower the compressive force.

With fairly accurate filling, only slight movement of the walls is required to produce balance. Thus, the gauge pressure is more nearly the internal pressure and the external fill acts only as a transmitting fluid.

Fills are adjusted as follows: A first approximate value can be obtained from the Tem-Pres apparatus by filling collapsible platinum tubes to various degrees with the proper base solution and Al_2O_3. The capsules are brought to operating temperature and the desired pressure applied. Observation of the capsule ends after the run will reveal the capsule which has just begun to swell but not burst. This fill is then the first to be tried in large systems. The corresponding external fill is gotten from Kennedy's Tables.[6]

Fine adjustments are made afterwards by observation of the physical conditions of the can after each run.

2.3.3 Can Extractor

Because of improper pressure balance or slow leaks in the entire system, there would occur in some cases a puffing up of the silver can. Due to the proximity of the autoclave walls, this expansion could not proceed too far. The movement of the can's wall would be stopped by the autoclave walls. As a result of this large expansive force, the silver can walls would be forced against the autoclave making removal of the can extremely difficult.

While this situation was true of the small can and vessel, it is even a greater problem in larger cans (3 inch diameter). In order to remove the cans after a run, an extractor (Figure 14) was
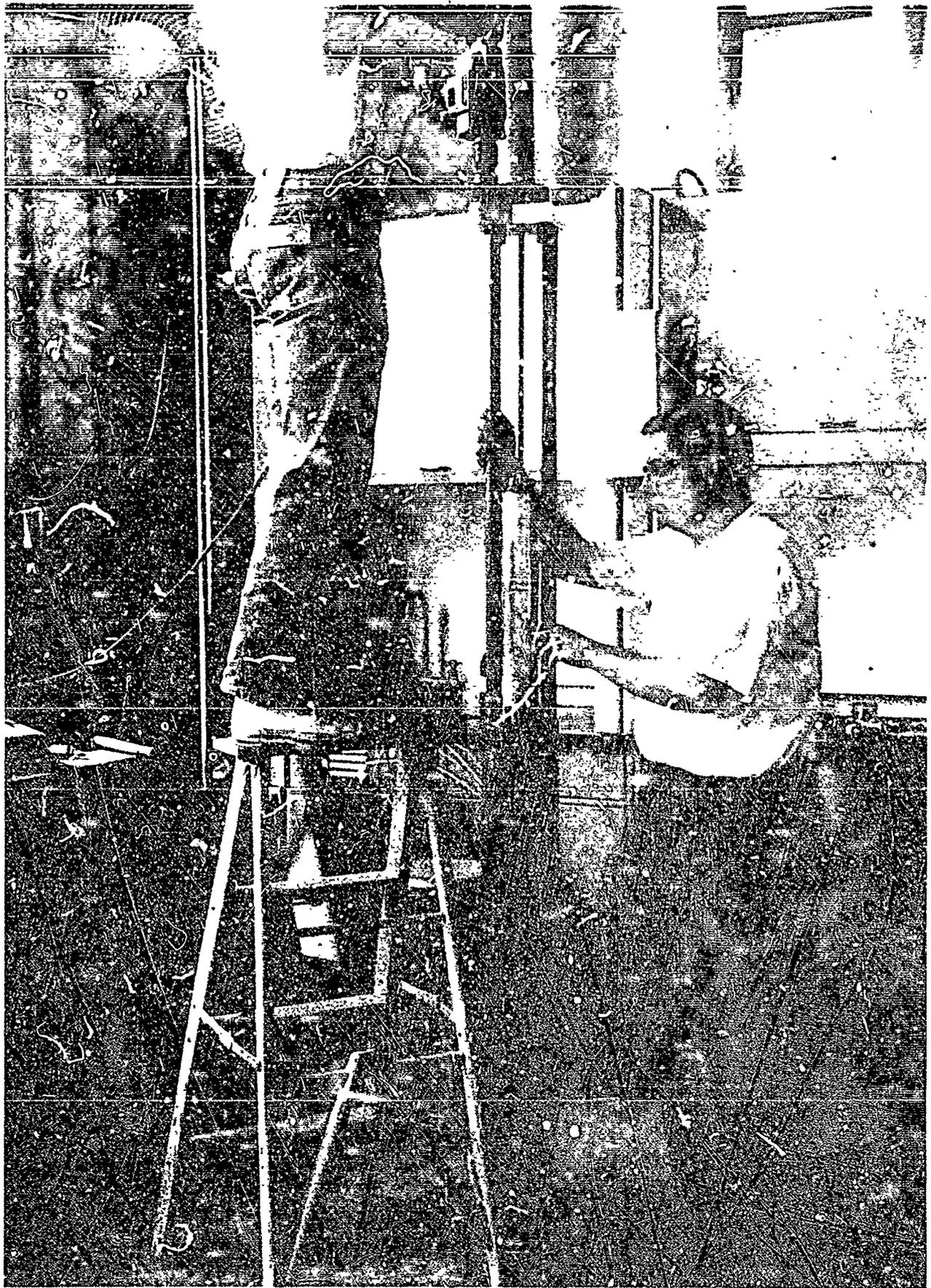
Figure 14 - Can Extractor

- 22 -

Pilot Line (Continued)

designed and constructed which could be used with both vessel sizes.
For the smaller can, a large screw was threaded into the top cap to pro-
vide a clasping handle. The cap of the larger cans were provided with a
large nut for easy removal. After clasping this handle in either case,
the can is removed by driving the threaded rod with an electric drill.
This instrument has removed cans which appeared to be impossible to re-
move manually.

2.3.4 Seal Area Lapping Tool and Polishing Tool

In order to regenerate and polish the sealing surface
of the autoclave properly, it was necessary to design and develop two
tools, - the final models of each are shown in Figures 15 and 16.

The lapping tool is made so as to generate a surface
of the proper sealing angle (7°) whose bore was concentric with that of
the threads This particular alignment was found to be necessary since
the bore used for the threads and that of the autoclave body are not neces-
sarily uniaxial. Deviation from this geometric configuration leads to
seal leaks The lapping section of the tool is made of cast iron; the
surface of the lap is regenerated periodically by milling. The guide in
the body of the tool is made of aluminum and is fitted for one vessel
specifically and used only for that vessel thereafter.

A polishing tool was also developed to be used after
the seal surface had been ground with the lapping tool. The mirror
polish produced by this tool was found to be essential in order to seal
the autoclaves for use at combinations of high pressure-temperature con-
ditions (>500°C - 20,000 psi). In this case, after the autoclave has
been suitably ground with the lapping tool, the polisher is placed in the
seal area and driven at high speed by an electric drill. With experience,
mirror finishes are easily attained in a matter of 2 to 3 minutes. No.
320 aluminum oxide abrasive is suspended in an oil slurry and used for
both the lap and polisher.

2.4 Operational Procedures

2.4.1 Tem-Pres Procedures

Platinum capsules of two sizes. 1.5 inches long x 1/4
inch diameter tubing, 0.005 inch wall are used for solubility work and
4 inch long tubes of the same platinum for crystal growth.

The capsules were fabricated by crimping and welding
in a chuck which also serves as the negative terminal and thermal sink
while welding the capsule seams Spectrographic carbon rod 0 125 inch
diameter sharpened to a point and held in a pin vise forms the positive
electrode. Power for the welding operation is provided by a variable
voltage (0 - 200 volts) filtered, 20 ampere power supply, which is more

- 23 -
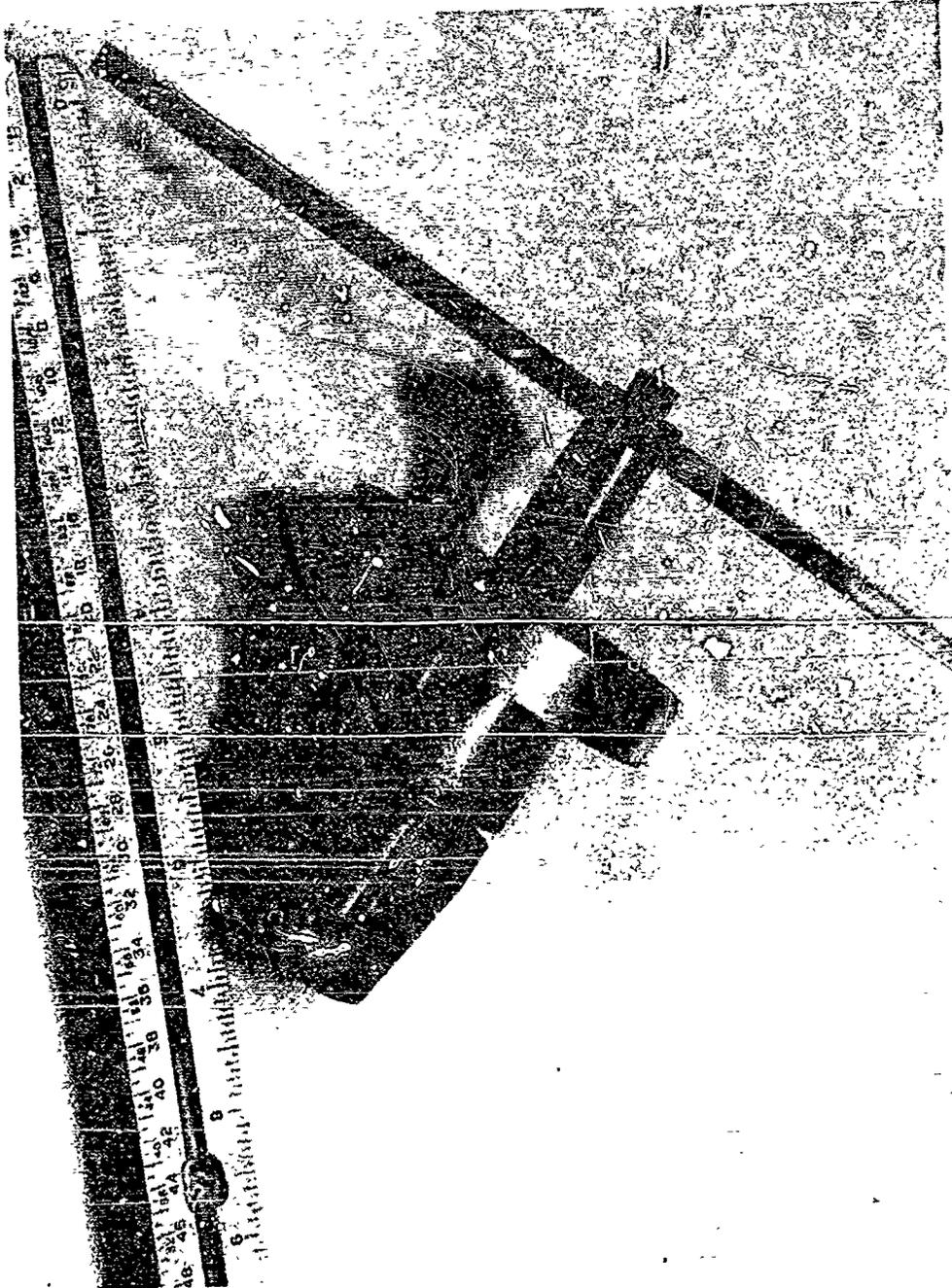
Figure 15 - Grinding Tool for Autoclave Seal Surface

Steel Drive Shaft

Properly Tapered Aluminum
Lap Block

No. 320 Emery Paper
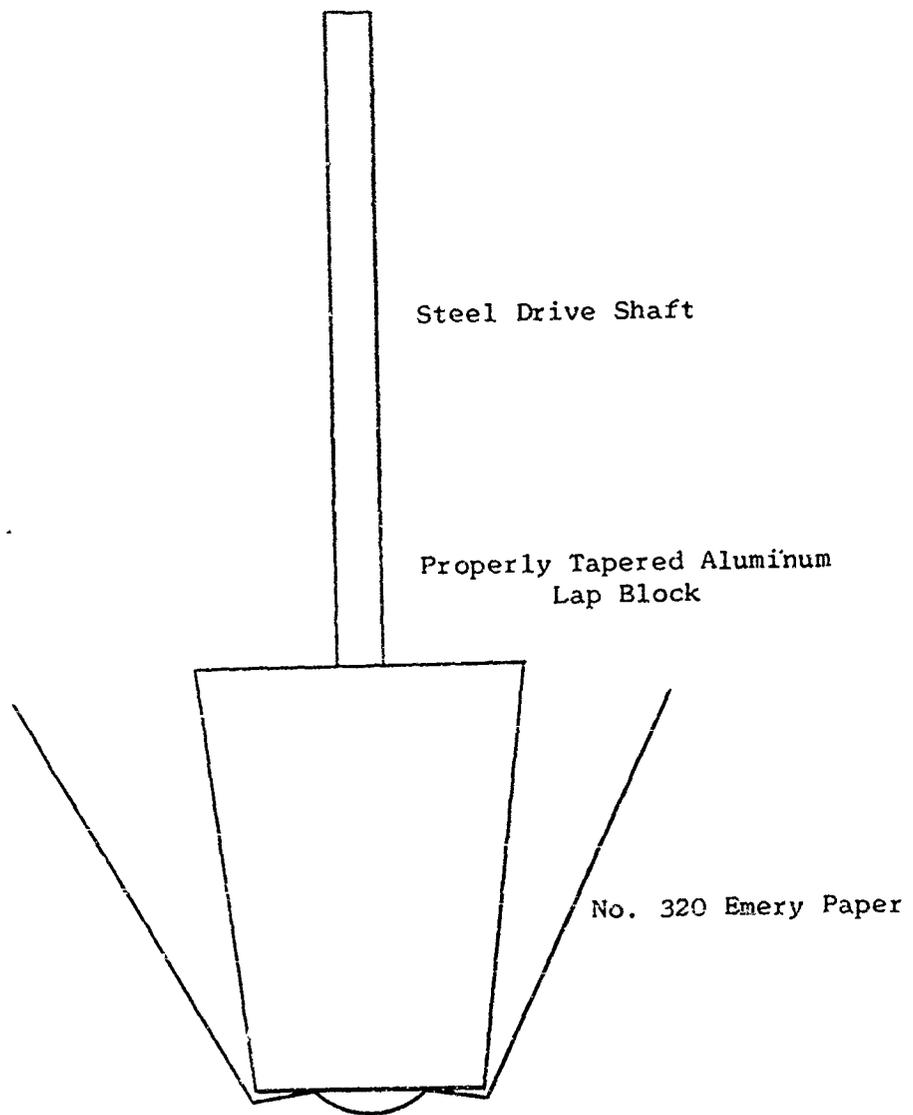
Figure 16 - Autoclave Seal Surface Polishing Tool

Pilot Line (Continued)

than ample to weld 0.005 inch platinum. Crimping was performed in a
three-jaw universal chuck designed for a miniature lathe. (The tech-
nique and equipment designs were described by E. D. Kolb.[9])

To prepare the capsules, the procedure is:

1. Cut the platinum tubing to length (either
1 1/2 or 4 inch sections).

2. Clean with soap and water and rinse in tap
water.

3. Boil in concentrated hydrochloric acid.

4. Rinse in overflowing tap water followed by
several deionized water rinses.

5. Anneal (oven at $1000^{\circ}C$ for 15 minutes).

6. Place in chuck and crimp.

7. Weld end closed.

8. Examine under microscope.

Figure 17 shows three stages in the preparation of such
a hydrothermal capsule.

The solutions were prepared by weighing samples of re-
agent grade potassium carbonate and adding them to weighed amounts of
water. Solutions were prepared gravimetrically because the concentra-
tion is not a function of temperature when expressed gravimetrically.
It is a function of temperature when volumetric units are used.

A typical example of preparation of solution is:

1. Weigh 250 grams of deionized water.

2. Weigh 172.75 grams of reagent grade K_2CO_3
(5/4 mole) to prepare 5 molal solution.

3. Add K_2CO_3 to water and mix thoroughly.

4. Store in polyethylene bottle.

The samples for the solubility determination sections
of this work were cut from flame fusion sapphire rods 0.100 inches in
diameter. About 0.65 inch lengths were used. The rods were prepared
by the following procedure:

1. Boil in alcohol.

Steel Drive Shaft

Properly Tapered Aluminum
Lap Block

No. 320 Emery Paper
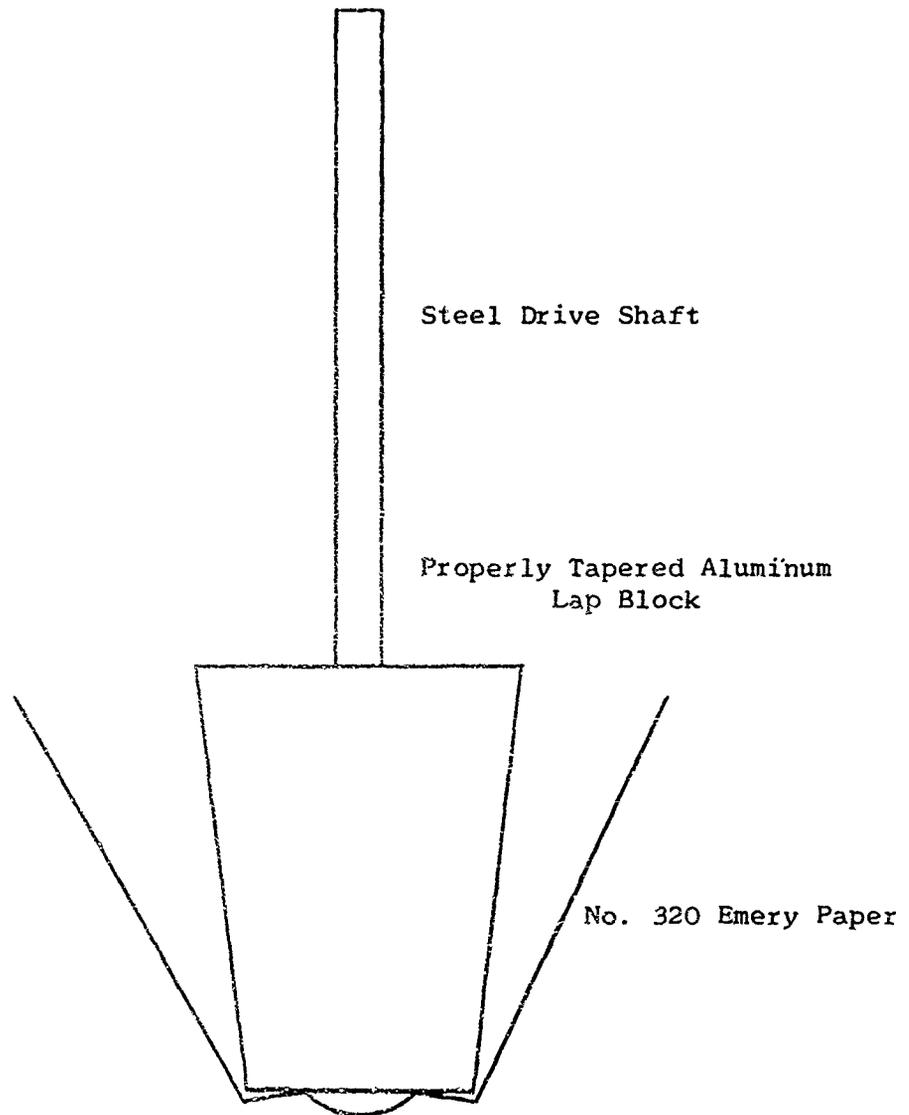
Figure 16 - Autoclave Seal Surface Polishing Tool
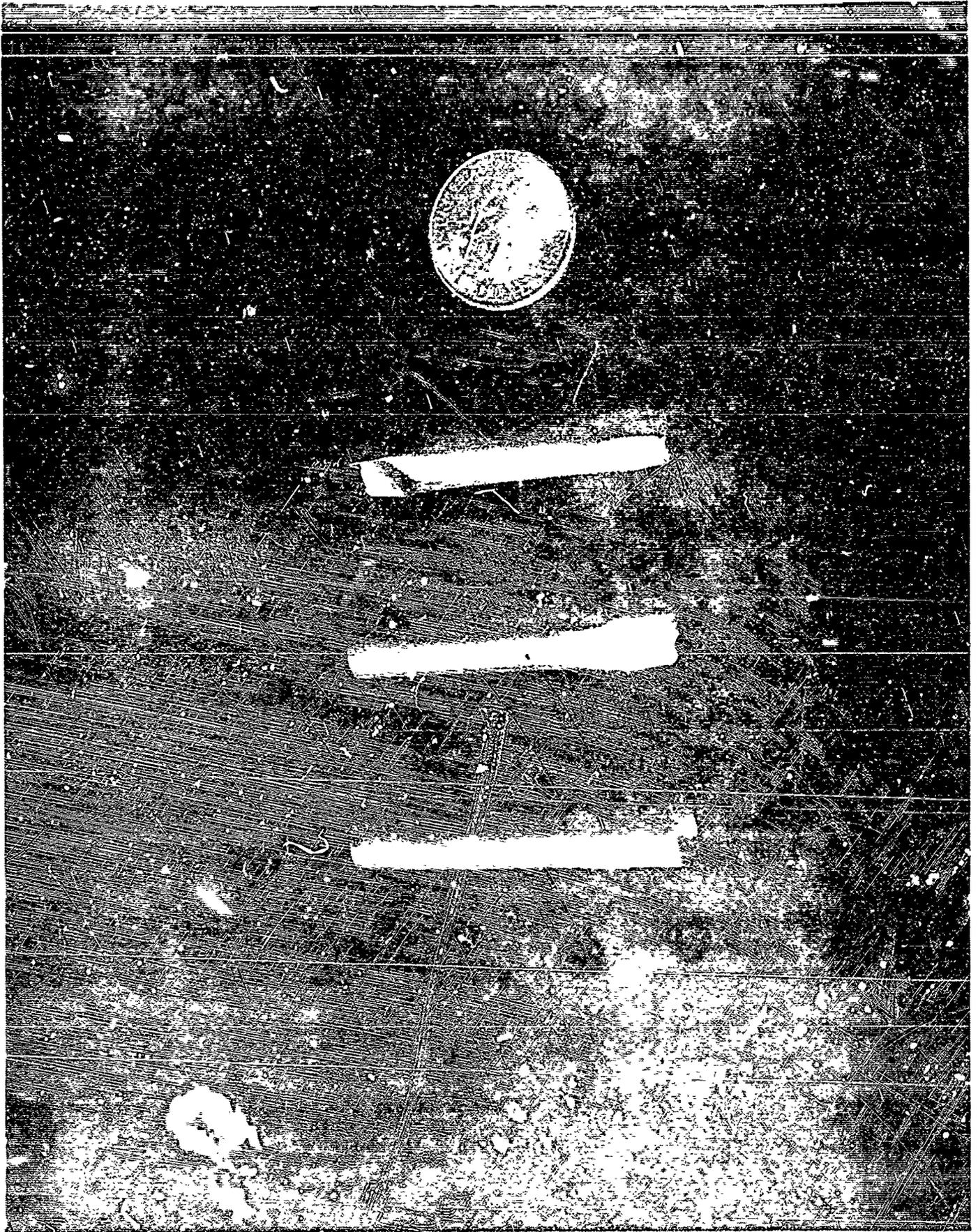
Figure 17 - Stages of Platinum Capsule Preparation

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Pilot Line (Continued)

      2. Rinse in water.

      3. Boil in HCl.

      4. Rinse in tap water followed by deionized water.

      5. Vacuum dry.

When the rods, capsules and solvent had been prepared, the capsule for a solubility determination was made up as follows:

      1. The 1 1/2 inch long platinum capsule was weighed to 0.001 grams.

      2. The sapphire rod was weighed to 0.0001 grams.

      3. The rod was placed in the capsule.

      4. The mineralizer solution (about 0.8 cc) was measured into the capsule using a hypodermic syringe.

      5. The capsule was weighed to determine weight of solvent (mineralizer).

      6. The capsule was welded shut.

      7. The sealed capsule was weighed.

      8. The capsule was placed in a Tem-Pres reactor and the reactor was filled with deionized water.

      9. The reactor was attached to a station of the research apparatus.

      10. The preheated furnace was placed in position.

      11. After twenty (20) hours, the run was quenched (first air, then water).

      12. The capsule was removed from the reactor and washed, dried and weighed (a change in weight indicated a leak).

      13. The capsule was opened (cut with a razor blade).

      14. The sapphire rod was cleaned, dried, and the weight change calculated.

Pilot Line (Continued)

15   From the weight loss and the weight of min-
eralizer, the weight percent solubility was calculated.

$$\frac{W_I - W_F}{W_{soln.}} \times 100 = \frac{\Delta W}{W_{soln.}} \times 100 = \% \text{ Solubility}$$

The procedures for small crystal growth runs in the Tem-
Pres were as follows, except for the preparation of capsules and Al_2O_3
preparation which were the same as above. The nutrient, about 1 gram of
scrap flame fusion material, was weighed on a semi-microbalance and placed
in the weighed platinum capsule. The solvent was measured into the cap-
sule by using a hypodermic syringe as a microburet. The usual amount was
about 1.5 milliliters. The capsule was again weighed to determine the
weight of solvent. The seed (a sapphire rod) was weighed and tied with
a 0.010 inch diameter platinum wire This wire was bent over the top of
the capsule to hold the seed in place. The top of the capsule was then
crimped and welded to seal the sample. The sealed capsule was placed in
one of the Tem-Pres reactors. The reactor was filled with deionized H_2O
and closed with 50 ft. lbs torque using a torque wrench. The reactor
was attached to the Tem-Pres pressure system and the preheated furnace
was raised into position. In about 15 minutes the furnace had reached
temperature and pressure equilibrium. The bottom of the reactor was
maintained at 500°C as measured by a thermocouple located in a well on
the side of the reactor near the nutrient zone. From previous measure-
ments of the gradients in the Tem-Pres furnaces, the growth temperatures
were about 430°C. No thermocouple wells were provided at the seed region
of the reactor. Growth was allowed to go on for about 60 hours (over a
weekend).

In operation the sealed capsule is placed in a reactor
which is mounted in a position on the apparatus. In most cases, about
80 percent of the final pressure is applied by means of an external
hydraulic water pump before the heating is begun in order to prevent
bursting of the capsule As the reactor temperature increases so does
the pressure. Final adjustment is made when the final operating tem-
perature is reached.

At the end of the experiment, the furnace is turned off
and the reactor allowed to cool under pressure. Crystal growth and solu-
bility data are then obtained by microscopic observation and weight loss
or gain measurements.

2.4 2   Preparation of Large Crystal Growth Autoclaves

After each run in the autoclaves, it is necessary not
only to thoroughly clean the vessel but also to renew the sealing sur-
faces and angles. The vessel cavity is scrubbed with a large diameter
($\sim$ 2 inch) brush and liquid detergent; it is then rinsed by flushing
with tap water and dried by a stream of compressed air. The pieces are
renewed as follows:

2.4.2.1 Seal Ring

After each run, it is necessary to machine the tapered surfaces of this piece because of the plastic deformation produced by the high pressure-temperature conditions to which it is subjected. As a result of this machining to diametrical and angular specifications, the height of the ring is shortened each time and it becomes necessary to replace it when it will no longer seal effectively. The finish on the seal after machining is produced by polishing it with No. 320 grit paper.

2.4.2.2 Cover Piece

This piece does not usually require machining; however, it is placed in a lathe and the seal surface polished with No. 320 emery paper after each run.

2.4.2.3 Seal Surface of Body

The seal surface of the autoclave is ground with the cast iron lap, (Figure 15), using No. 320 abrasive and finally No. 500 until all seal traces of the former run are removed. The lap must be milled frequently to its original specifications in order to insure generation of the proper sealing angle of the vessel wall.

Finally, the seal surface is polished to a mirror finish using the high speed lap and No. 320, wet or dry, emery paper.

All pieces are then cleaned with detergent to remove oils and grease. After drying the threads on the main nut and autoclave body, they are closely inspected for foreign material; e.g., burrs, which can later gall these threads.

2.4.3 Preparation of Silver Can - Loading of Autoclaves

The various parts of the cans and seed rack were constructed circles, tubes and rods of fine silver. After the appropriate cutting or milling, the pieces were welded together in an argon atmosphere. No flux or solder is used. Just prior to loading the cans for a run, the silver pieces were cleaned of grease and oil with detergent, washed with concentrated HCl, thoroughly rinsed with deionized water and then allowed to dry.

Seed crystals were suspended on the ladder by means of 20 mil fine silver wire attached to the seed by means of a notch or drilled hole in the seed. The seed rack was placed in the can and the top cap welded. Based upon a calculated void volume, the correct fill of K_2CO_3 solution was then placed in the can by means of the small vent pipe through the top. The fill is determined in accordance with the procedures given on Pages 17 - 23. The vent pipe was then crimped shut and welded.

Pilot Line (Continued)

The can was then placed in the autoclave, along with the appropriate external fill of deionized water. The vessel was then closed and placed in the furnace ready for operation.

2.4.4 Warm-Up

Three different warm-up schemes were used in the course of this work: (a) programmed, (b) "as fast as possible", and (c) a combination of (a) and (b). The programmed procedure was used only in the early part of this work when the operating pressure was 10,000 psi In this case, the vessel was heated at a constant rate to operating conditions over 24, 48 or 96 hours by using the temperature programmer modification on the West Controller. In most cases, all small seeds were completely dissolved away and the large ones were severely etched. The later work at 20,000 psi would indicate that the use of this procedure, at this pressure, would lead to the same result.

Drastic seed dissolution was prevented by heating the vessel to operating conditions "as fast as possible". This was accomplished by having the power inputs on the controller fixed at their ultimate position for operation and then switching on the controller

Operating conditions were approached within 2 - 3 hours with an additional 3 - 4 hours required for the entire assembly of furnace, vessel, etc. to attain thermal steady state. While this procedure prevented seed dissolution, the resultant crystal quality did not improve the fast and programmed warm-ups.

The description of the warm-up procedure used for these runs follows and is also shown diagrammatically in Figure 18. The sealed autoclave is heated "as quickly as possible" to an autoclave average temperature (see Page 17) of about 470°C. At these temperatures, the pressure is about 14,000 psi to 17,000 psi and the system is in what we believe to be a condition where slow growth occurs (~ 9 mils per day). This initial heating takes 3 to 4 hours to accomplish. The autoclave is held at these temperatures overnight, allowing the crystal to grow at slow rates. After about twenty hours in the "hold" condition, the temperature is programmed to the final set of operating temperatures (500°C to 525°C) over a twenty-four hour period bringing the pressure into the 22,000 - 27,000 psi range. These pressure-temperature conditions are those for high growth rates. High quality crystals were produced in the three runs cited using this warm-up procedure. For purposes of crystal growth, these runs lasted 2 - 7 days depending upon anticipated growth rates and run performance.

2.4.5 Shut-Down

At the end of the run, the power is switched off and the autoclave is air cooled; when zero gauge pressure is indicated, cold water is then passed over the vessel until it reaches room temperature.
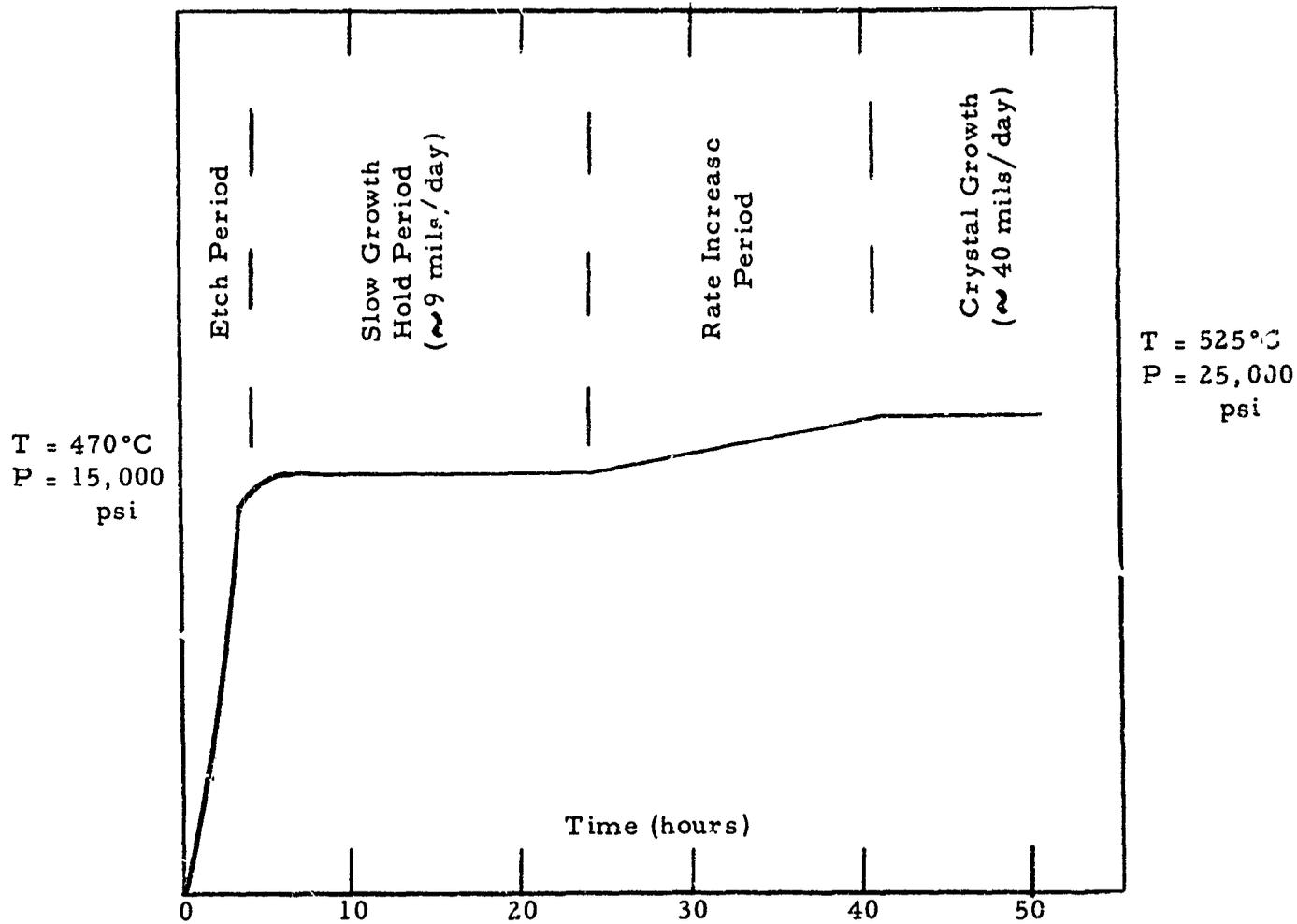
Figure 18 - Schematic of the Modified Warm-Up

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Pilot Line (Continued)

The vessel is opened with the main nut released by the opener (Figure 12). The silver can is removed manually from the auto-clave or with the extractor (Figure 14). The cap is sawed off, the ladder removed, and the crystals cleaned and measured.

Cleaning of the crystals in most cases entailed removing a thin coating of diaspore (AlOOH) from the crystal surface by scraping them with a stainless steel spatula. This coating forms due to crystallization as the P-T conditions of the reactor pass through the diaspore region of stability.

3.0 GROWTH RESULTS

3.1 Solubility and Preliminary Growth Results

The data collected for the solubility of sapphire in K_2CO_3 are given in the Tables in Appendix I and are also represented by the accompanying Figures. The solubility is calculated as the Al_2O_3 weight loss x 100/weight of water + weight of K_2CO_3. The variation of the solubility with the varying parameters did not exhibit anomalous behavior in any way. From the data, the temperature coefficients of solubility $\Delta S/\Delta T$ were calculated and are presented in Table I. From the data in this Table, one would conclude that hydrothermal crystallization of sapphire from 2 - 7 m K_2CO_3 at any temperature above $400°C$, the diaspore to corundum phase transition temperature, should merely be a matter of imposing a temperature gradient on the system. From such data, however, the growth rate cannot be predicted. The data also indicated a high degree of solubility for sapphire at modest pressures, 5,000 - 10,000 psi, and that this high solubility appears to be virtually independent of pressure from 5,000 psi to 30,000 psi.

TABLE I

TEMPERATURE COEFFICIENTS OF SOLUBILITY AT VARIOUS MINERALIZER CONCENTRATIONS

Concentration	$\Delta S/\Delta T$ (%/°C)
2 molal	0.015
3 molal	0.018
4 molal	0.024
5 molal	0.029
7 molal	0.030

Later, work in the large systems indicated that the conventional manner of expressing hydrothermal solubility; that is, weight percent, while convenient, can lead to erroneous conclusions. That is because the capsules are extremely compressible, having no fixed volume. As a result, the pressure in the capsule is fixed by the applied pressure. The density of the solution is due to the amount of solvent in the capsule, extent of solution of the sapphire sample and the compressibility of the fluid at the conditions of measurement.

In the large systems, on the other hand, the volume is nearly constant and, in order to change the pressure at constant temperature, it is necessary to change the degree of fill. Increasing the fill increases the fluid density, solubility, and thus, the Al_2O_3 content per milliliter of fluid.

Growth Results (Continued)

From the weights of seeds and nutrient before and after a run, the weight change calculation and volume correction can be m e. Since the volume of the can is known and the amount and density of fill are known, the volumetric concentration may be calculated. Unfortunately, this work was done under non-isothermal conditions during crystal growth runs. however, the validity of this proposed method of representing solubility is not affected since the average temperature for the runs in question were all the same.

The solubilities are at best only an approximation of the solubili y at the average temperature of the vessel. The data are presented in Table II and Figure 19. The maximum in the curve was somewhat surprising in that either a continued increase or leveling off would be expec d. The fact that the point labeled No. 104 is far off the curve is explicable since in that case the silver can leaked, diluting the base concentration with a resultant decreas in solubility. The behavior of the curve above 25,000 psi is not presently understood.

TABLE II

VOLUMETRIC SOLUBILITY OF Al_2O_3

Run No.	Pressure (psi)	Fill (grams)	Corrected Volume (ml)	Weight Loss (gms.)	$\dfrac{\text{Mole } Al_2O_3/\text{Mole } K_2CO_3}{V_{corr.}}$
93	27,300	389.3	317.6	35.7	6.370×10^{-4}
96	22,200	377.6	306.9	28.7	5.464×10^{-4}
98	29,100	365.9	298.4	32.4	4.52×10^{-4}
101	25,300	377.0	308.4	38.6	7.325×10^{-4}
104	24,000	387.9	315.0	27.7	5.000×10^{-4}
105	22,700	387.2	315.0	31.0	5.606×10^{-4}

It is obvious that more work of this nature is req ired in the future to develop fully this concept of hydrothermal solubility and to relate growth rates and quality to the density of these fluids.

Based on the solubility work in the small capsules, several crystal growth runs were carried out in the small apparatus using flame fusi n sapphire rod as seeds. Several runs were made to grow ruby using K_2CrO_4 to dope crystal or with ruby as nutrient.

A sampling of t se crystals are shown in Figure 20 and the conditions under which they were grown are presented in Appendix II. From these results, it appeared that ruby would be grown quite easily in K_2CO_3 solutions at moderate temperatures and pressures.
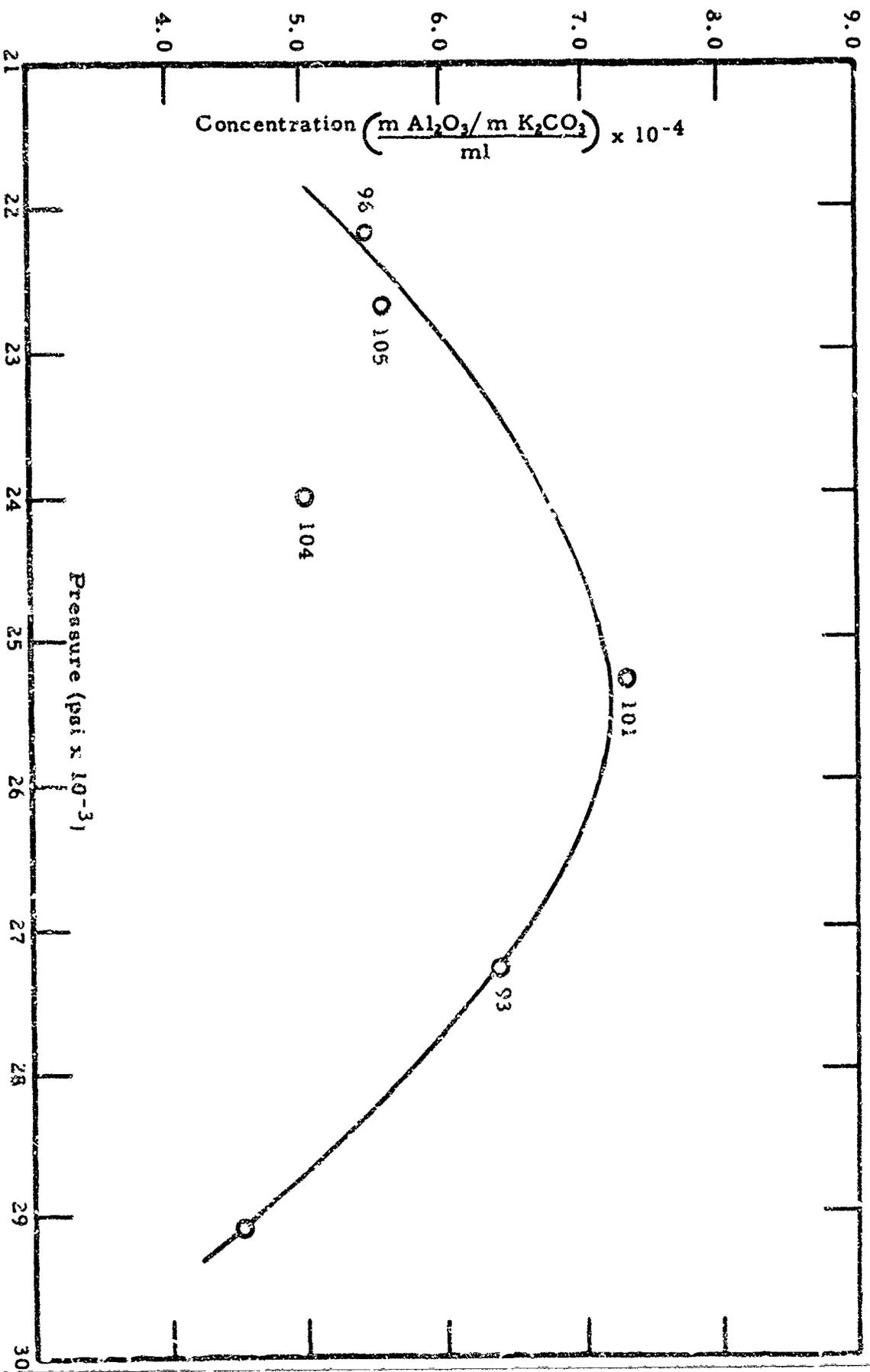
Figure 19 - Volumetric Solubility vs. Pressure

Figure 20 - Ruby and Sapphire Crystals Grown in Tem-Pres

Growth Results (Continued).

3.2 Results of Rate Studies and Crystal Growth in the Large System

3.2.1 Early Growth

Using the solubility and growth data from the small capsules as guides, crystal growth was now attempted using welded silver cans in the large autoclaves. Since growth had been obtained so readily at 10,000 psi with 4 m K_2CO_3, and at suitable rates   mils per day), there did not appear to be any reason to use higher   king pressures.

Crystallization temperatures of 395 to 440°C were used and ΔT's of ˜0 to 250°C were attempted to induce high degrees of super-saturation. These early attempts at crystal growth in the large system at 10,000 psi, 4 m K_2CO_3 were near satisfactory. Many times the small seeds would completely dissolve and larger seeds would be severely etched. When growth did occur, the rate was always quite low, 10 mils per day or less. In any case, data and observations in later runs in-dicated that, under the early conditions, there may have been two fluid phases present. The two high pressure phases acted in much the same manner as two immerscible liquid phases at room temperature; e.g., water and n-butanol. Instead of being strongly temperature dependent, these two phases appear to be pressure and solvent concentration dependent as manifested by the crystal growth rate variance with these parameters.

3.2.2 Rate vs. Solvent Concentration at 10,000 psi

The conditions and results of all crystal growth runs are presented in the tables of Appendix III.

The first of these parameters to be investigated was the effect of solvent concentration on rate in the <$10\bar{1}1$> direction using 4 m K_2CO_3 at 10,000 psi and 450°C; the data is shown in Figure 21. It is apparent that little or no growth should occur at solvent concen-trations of greater than about 3 m K_2CO_3. Indeed, this has been found to be the case.

Evidence of a meniscus line was revealed upon examin-ation of the interior surfaces of the silver cans after runs at low molalities. This meniscus would, of course, be indicative of a two-phase fluid and thus support the hypothesis.

3.2.3 Rate vs. Molality at 20,000 psi

Based upon the results obtained at 10,000 psi and in an attempt to improve crystal quality, a series of runs was made at 20,000 psi with varying K_2CO_3 molality at 450°C and with <$10\bar{1}1$> and <0001> growth oriented seeds. The data for this series of runs are shown in Figure 22. In this case, there are two curves representing rate of growth in either <0001>, "c", crystals obtained from molten
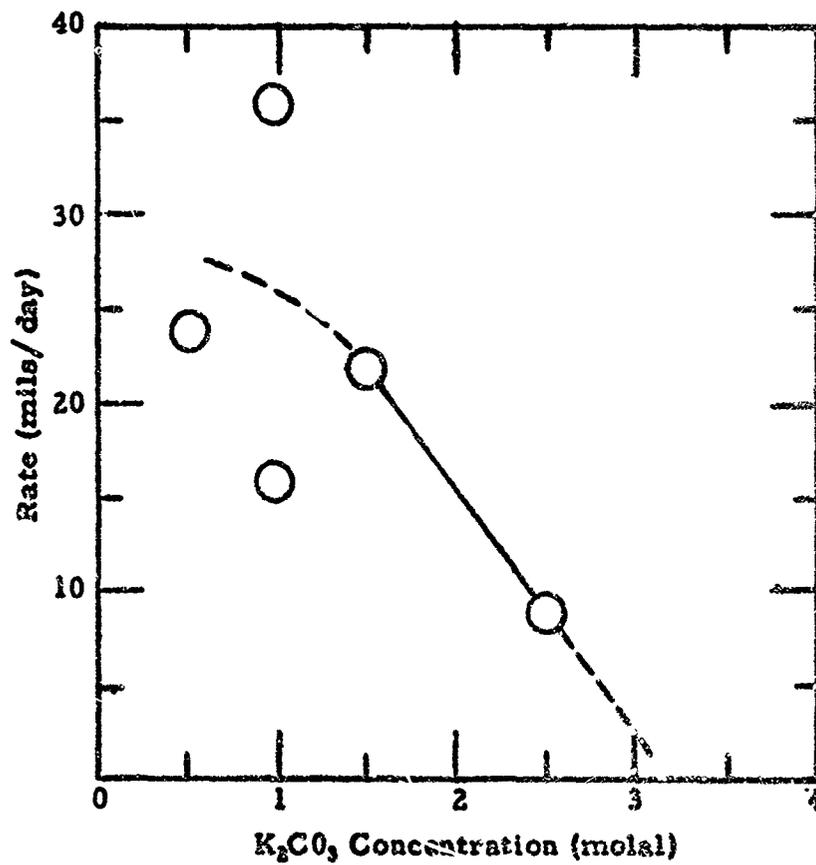
Figure 21 — Growth Rate vs K_2CO_3 Concentration at 10,000 psi
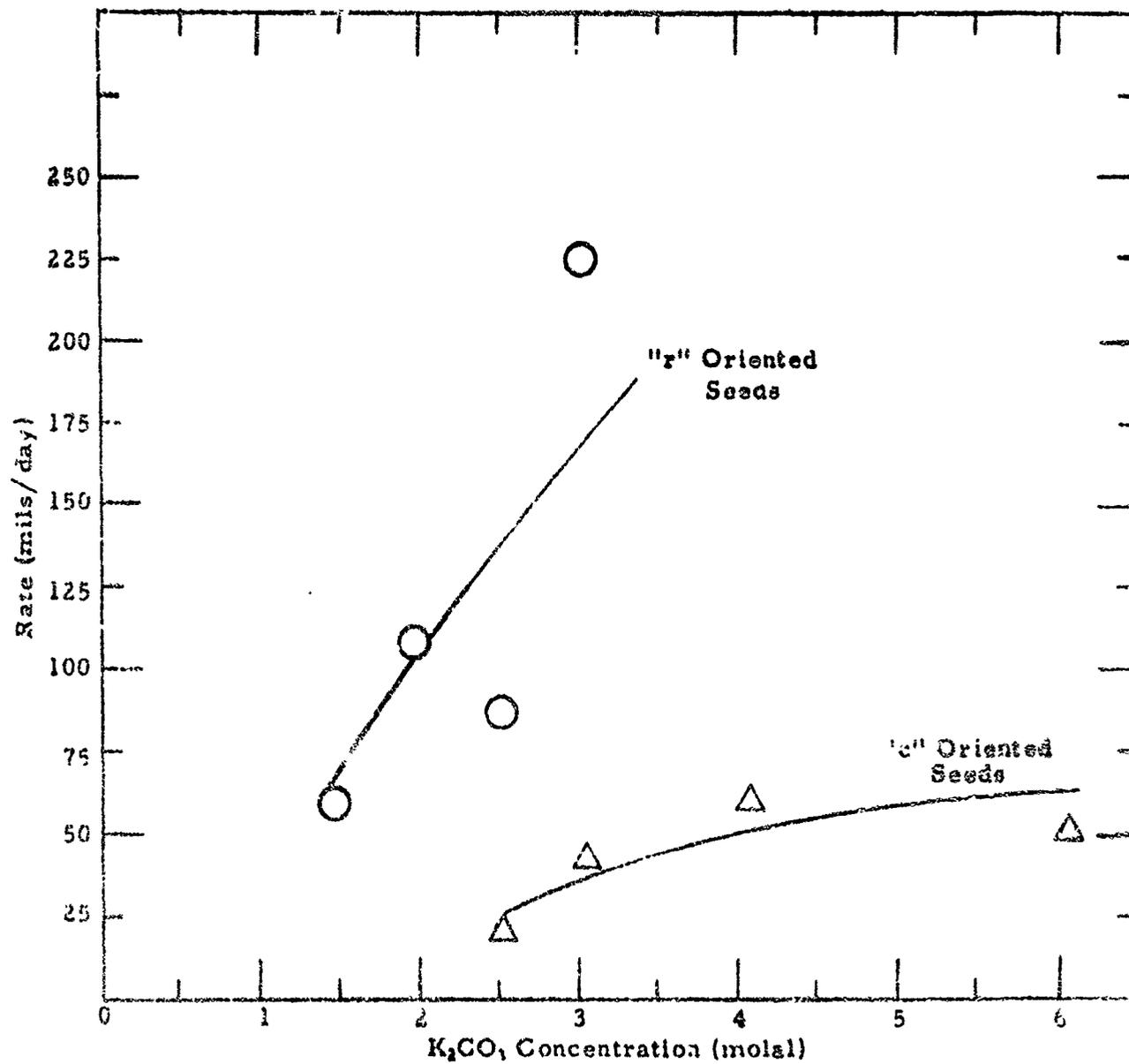
Figure 22 - Growth Rate vs. K_2CO_3 Concentration at 20,000 psi

Growth Results (Continued)

salt or on flame fusion crystals with growth in the <$10\bar{1}1$>, "r", direction. In the case of "r" oriented crystals, comparison should be made with the results at 10,000 psi. Not only are the rates much greater but the shapes of the curves are entirely different. The curves obtained for the data at 20,000 psi are more near to what would be predicted for a hydrothermal system; whereas, the 10,000 psi data are very difficult to explain.

One possible explanation of this difference would rest in the two fluid phase systems at low pressure versus one phase system at the higher pressure. The second feature of the rates found under these conditions are that they are 4 - 5 times greater than those reported by Laudise[2] for sapphire in Na_2CO_3. Laudise reported a rate of 10 mils per day in the <0001> direction at 30,000 psi and 400°C - 450°C using Na_2CO_3 as a "mineralizer".

The discovery of the high growth rate at high pressures was very significant in contributing to the success of the growth of large crystals. Although rates of about 40 mils per day had been attained at 10,000 psi, this growth was in the <$10\bar{1}1$> direction which is a fast growing direction. On the other hand, at 20,000 psi, rates of 40 mils per day were also obtained but in the <0001> direction, or a slow growth direction. The factor of crystal quality as a function of growth direction and seed origin will be discussed later; however, without a reasonable rate of growth with high quality, the feasibility for future large crystal growth would be doubtful.

3.2.4 Rate vs. Pressure

The variation of rate with pressure has not been investigated thoroughly. Related data that were collected with only pressure as a variable are shown in Figure 23. The data collected at 14,000 psi and 17,000 psi were regarded as sufficiently close to pinpoint the pressure at which the rate drastically changes.

Since most of the later high pressure work was performed using 6 m K_2CO_3, we do not have any data at higher pressures than 20,000 psi for 4 m K_2CO_3. From our observations of the growth rates at pressures higher than 20,000 psi, and with 6 m K_2CO_3, we would conclude that the rate at high pressure is almost pressure independent. These observation would thus support results shown in Figure 23.

The cause of this step in the pressure rate is again believed to be due to the existence of a two-phase fluid system at low pressures and a single-phase fluid at high pressures. Undoubtedly, this transition and the pressure range over which it occurs is dependent on both the temperature and solvent concentration. This phenomenon must be investigated more thoroughly at a later date.
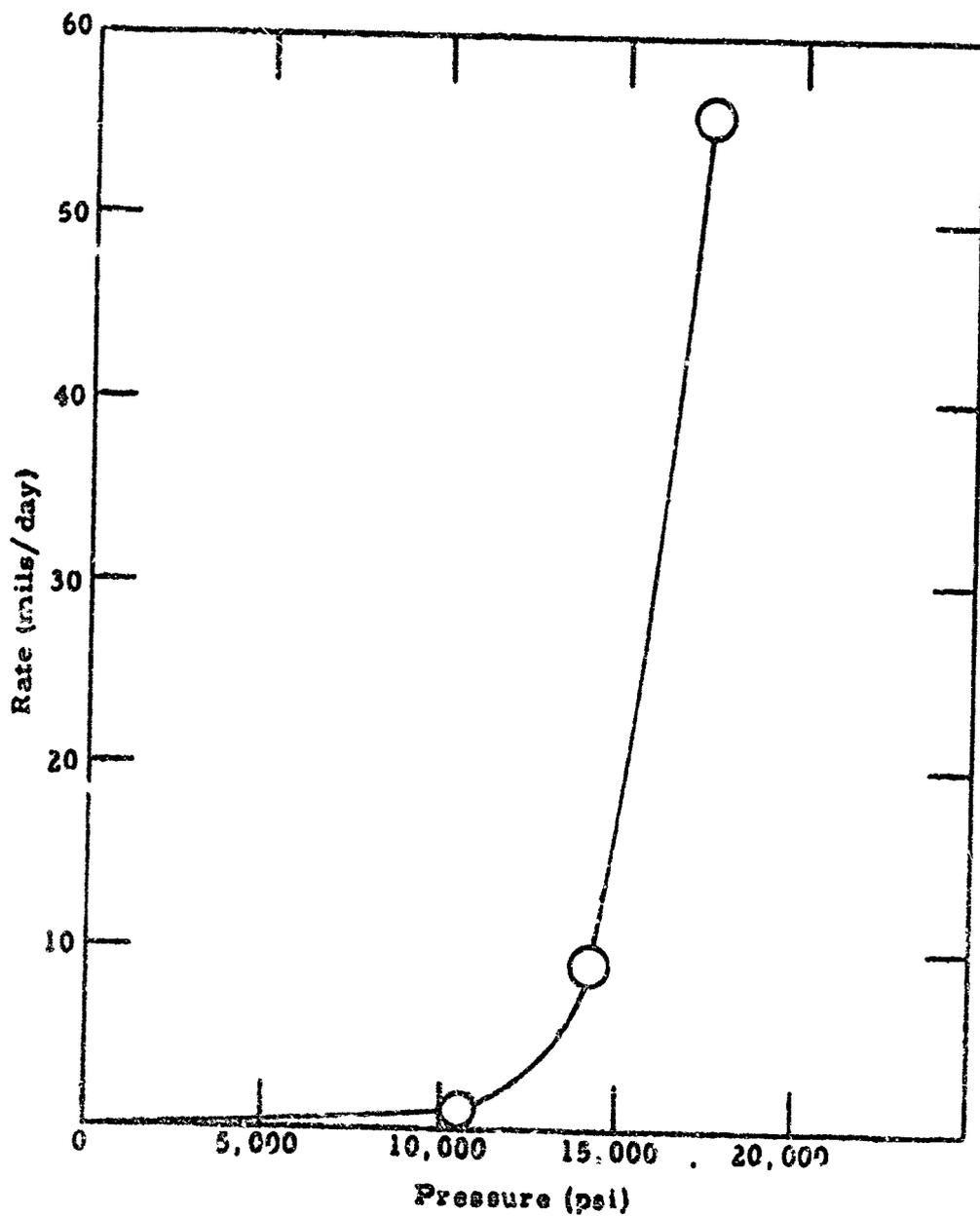
Figure 23 - Growth Rate vs Pressure (4 m K_2CO_3, "c" oriented Seeds)

Growth Results (Continued)

3.2.5 Rate vs. Temperature

As in the case of the pressure, the growth rate as a function of temperature was only observed secondarily as attempts were made to improve the crystal quality. As one would anticipate, the growth rate increases as the growth temperature is increased. The selected data, (pressure, molality, etc. held constant), are shown in Figure 24 and are plotted in an Arrhenius Plot in Figure 25. From this latter line, an activation energy of 16 Kcal was calculated. This is in the same neighborhood with several values reported by Laudise[10] for quartz dependent upon orientation and conditions. For the basal plane of quartz at 80 percent fill and 0.5 m NaOH, Laudise has reported a value of 20 Kcal. The similarity in values would suggest the same mechanism is rate controlling in both cases.

Of even greater interest would be a comparison of this value with an activation energy calculation for data at a low pressure; e.g., 10,000 psi. This would undoubtedly shed light on the possible existence of the two-phase system at low pressures and the single-phase system of pressures greater than 17,000 psi.

3.2.6 Rate vs. Orientation

No direct study was made of the effect of orientation on growth rate. However, the rates were measured in all cases and comparisons were made where possible. In general, the effect of various orientations on rate appeared to be similar to those reported by Laudise; i.e., the rate in the $<10\bar{1}1>$ direction was greater than that in the $<10\bar{1}0>$ direction. The $<10\bar{1}0>$ rate was about the same as the $<22\bar{4}3>$ which was greater than the $<11\bar{2}0>$. The $<0001>$ and $<11\bar{2}0>$ rates were almost equivalent.

$$<10\bar{1}1> \; > \; <10\bar{1}0> \; \cong \; <22\bar{4}3> \; > \; <11\bar{2}0> \; \cong \; <0001>$$

One further orientation was investigated and found to be faster growing than any of those in the above list. This direction was the $<10\bar{1}2>$.

3.2.7 Final Growth Conditions

The conditions established for the growth of high quality crystals at reasonable rates are as follows:

Solvent:	K_2CO_3	ΔT:	$5\,^{\circ}C$
Solvent Concentration:	6 m	Seed:	Molten salt
P:	25,000 psi		ruby
T_{cryst}:	525°C	Nutrient:	Scrap flame
$T_{nutrient}$:	530°C		fusion laser
			ruby
		Internal fill.	84%
		External fill·	65%
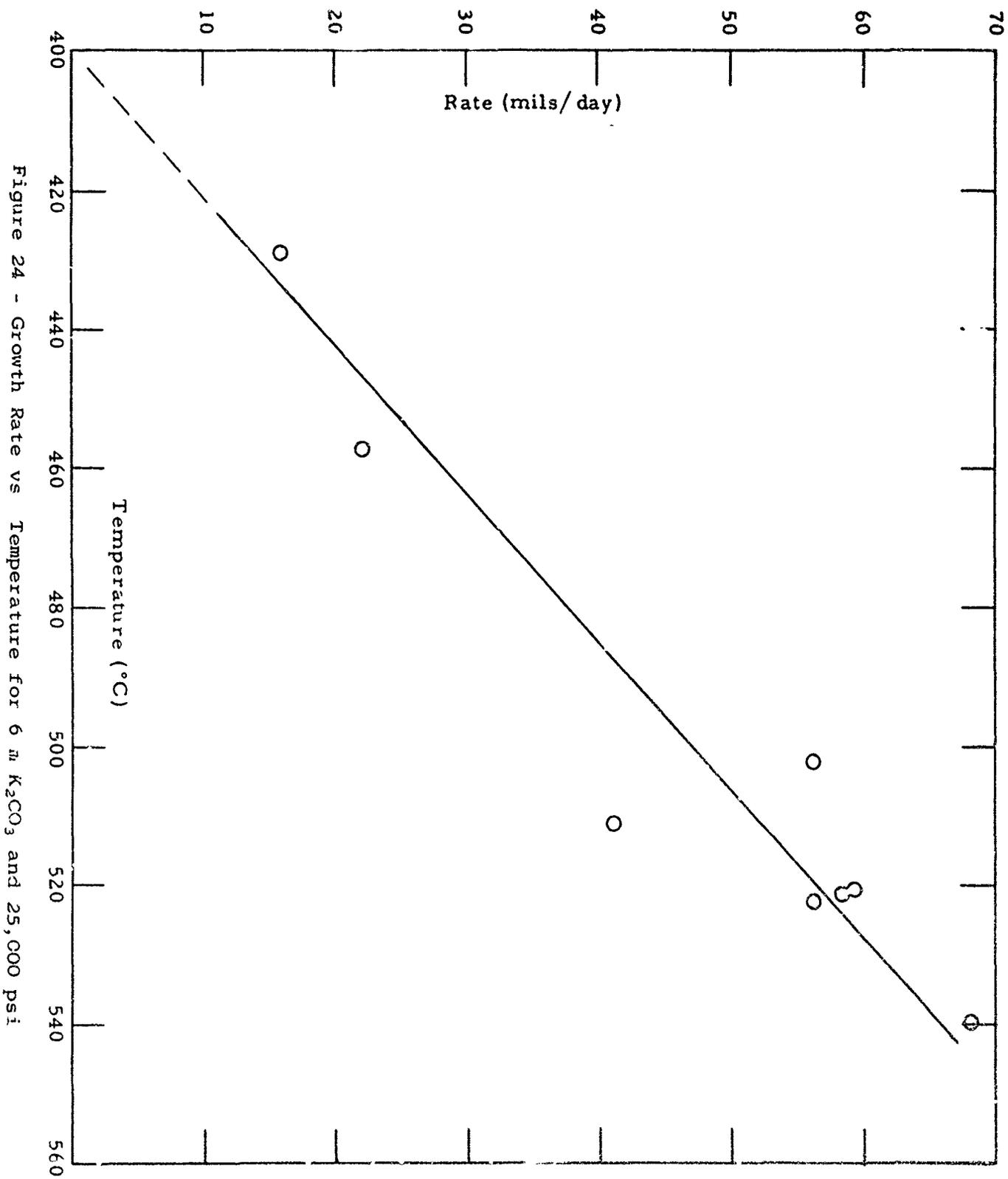
Figure 24 - Growth Rate vs Temperature for 6 m K_2CO_3 and 25,000 psi
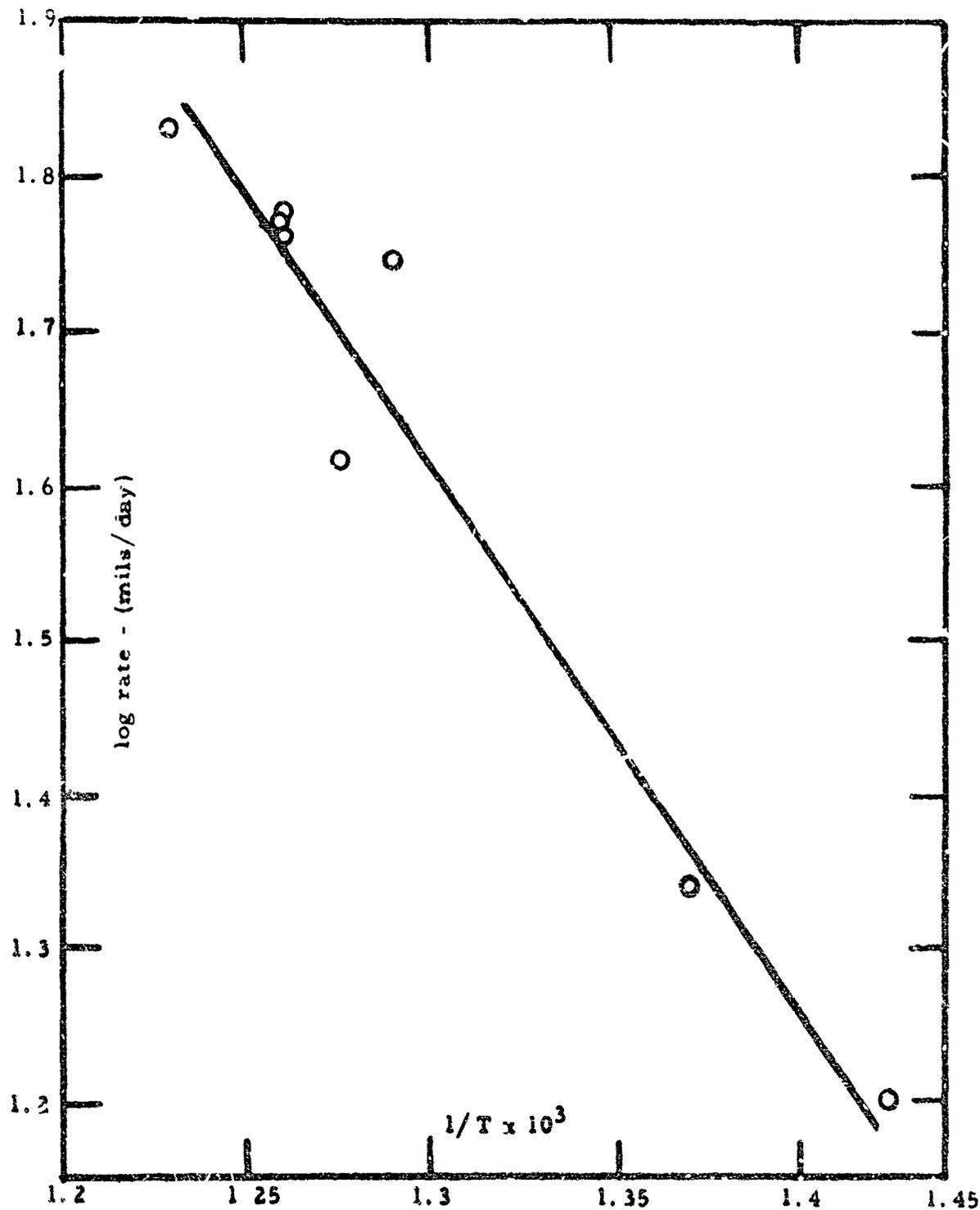
Figure 25 - Arrhenius Plot of Data for 6 m K_2CO_3 and 25,000 psi

4.0 CRYSTAL QUALITY AND TESTING

Once having obtained high growth rates at high working pressure, the main goal of the program was to grow high quality crystals. The macroscopic defects were so substantial that it seemed necessary to remove them before investigating and rectifying microscopic defects. Crevice flawing, non-uniform chromium deposition, veiling, and cracking were the major defects and are discussed along with the pertinent growth parameters in the following sections.

4.1 Crevice Flawing

Crevice flawing was observed with increased growth rate. This flawing was observed even at 10,000 psi but only when the solvent concentration was 0.5 to 1.5 m. Crevice flawing has the appearance of sharply, well defined mountain-like ridges and valleys; hence, the description, crevice flaw. The problem appears to be caused by supersaturation and can be lessened by lowering the supersaturation.

One factor worthy of note is the relationship between the propensity toward crevice flaws and orientation and that this relationship roughly corresponds to the rate and orientation combination. It appears that the flawing tendency decreases in the following order:

$$<10\bar{1}0> - <10\bar{1}1> - <10\bar{1}2> - <22\bar{4}3> - <0001>$$

with the <0001> showing the least tendency to flaw.

An example of this flawing and the general crystal quality, and morphology of crystals grown on variously oriented seeds is shown in Figure 26.

4.2 Banding or Non-uniform Chromium Deposition

The non-uniform deposition of chromium in the growth of a crystal causes regions of the crystal to be more deeply colored than others. In a cross-sectioned area, Figure 27, the regions appear as bands of light and dark material surrounding the seed. The banding has usually been apparent only at or near the beginning of the growth cycle. This band, we believe, is due to different temperature coefficients of solubility for the chromium oxide and aluminum oxide. Thus, while the Al:Cr ratio of dissolving material is fixed by the nutrient composition, under steady state conditions, the ratio in the growing crystal will be dependent on the alumina and chromia concentrations in the growth zone. These concentrations will be dependent upon the composition of the nutrient, the pressure, temperature and solvent composition. If the distribution coefficients involved are not unity, the ratio of chromium oxide to aluminum oxide must be adjusted by either a heavy deposit or lighter deposit on the seed. Both types of bands at the seed have been noted depending upon solvent concentration and warm-up cycle. In any case, after warm-up and establishment of steady state conditions, very little banding occurs. However, some fluctuations have been observed on occasion which may have been due to ambient temperature changes or slight changes in ΔT during the run.

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Figure 26 - Habit of Grown Crystals

Figure 27 - Cross Section Showing Chromium Banding

Crystal Quality and Testing (Continued)

Both warm-up procedures and solvent molality appear to be the parameters of greatest influence on the initial band. The warm-up procedure and effect on quality will be discussed in the next section. With regard to the effect of K_2CO_3 concentration, it appears that the higher concentrations tend to decrease the degree of banding.

4.3 Veiling and Cracking

The most serious problem in the growth of ruby has been that of veiling and cracking. The two defects are discussed jointly in that they occur together and appear to be interrelated.

Figure 28 shows a typical example of the appearance of a veil. The veils in ruby are somewhat different from those appearing in other materials; e.g., quartz, KDP, ADP, etc., but they are very similar to those seen in yttrium aluminum garnet grown from flux. At present, the exact cause of these defects in ruby is not known. They appear as filmy inclusions of solvent and crystallized solute. Their origins have not definitely been traced to any particular seed defect nor to any operational changes which might conceivably induce such a defect. It has been found that the amount of veiling can be greatly reduced or completely eliminated on molten salt seeds by a modification of the warm-up procedure. The procedure finally established is described on Pages 31 and 32. Figure 29 shows some of the crystals prepared using this technique.

4.4 Seed Orientation, Origin and Crystal Quality

The effect of orientation has already been discussed in conjunction with crevice flawing. For this reason, seeds whose major growth faces are <0001> have been found to be most suitable and those on which the highest quality crystals have been grown. Furthermore, it has been found that there is a vast difference in the quality of the crystal depending on the origin of the seed. Crystals grown in the <0001> but on flame fusion $0°$ boules have been shown by R. Barns of Bell Telephone Laboratories[11] to be almost polycrystalline. On the other hand, crystals grown in the <0001> direction but on molten salt seed plates were of very high quality.

The crystals grown on molten salt seed plates have in many cases appeared to be almost strain free, Figures 30 and 31. The strain which does appear in the crystals may arise at the seed interface and grown crystal due to lattice spacing differences between the molten salt and hydrothermal materials. Figure 33 shows the high optical quality of one such crystal which, when viewed with crossed Nicols, shows a strain pattern in the center of the crystal while the edges of the crystal are not strained. The original seed can easily be seen by comparative examination of the two figures.

At present, only molten salt seed plates have been used suc-
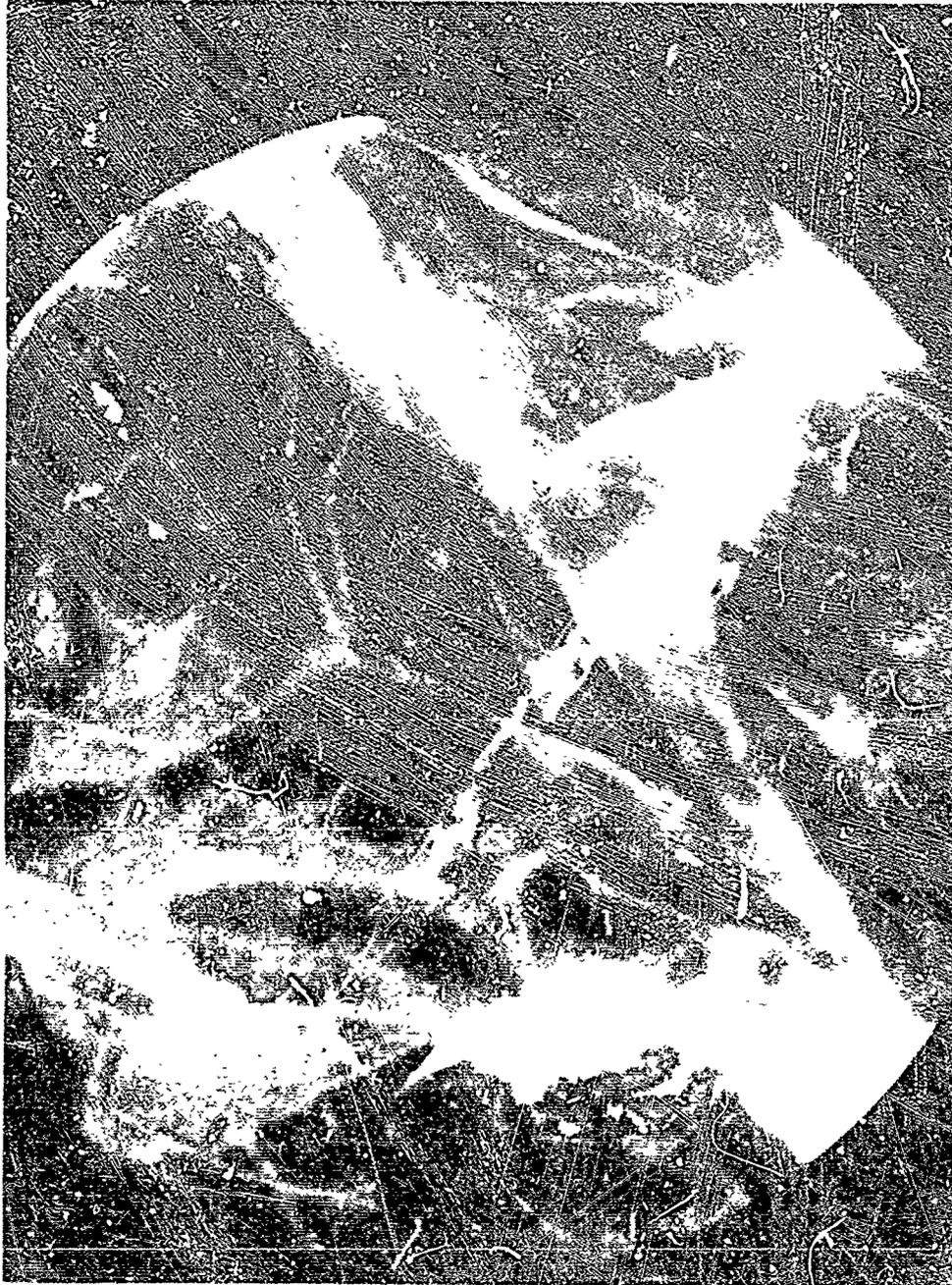
Figure 28 - Photomicrograph of Veiling in Ruby Crystal
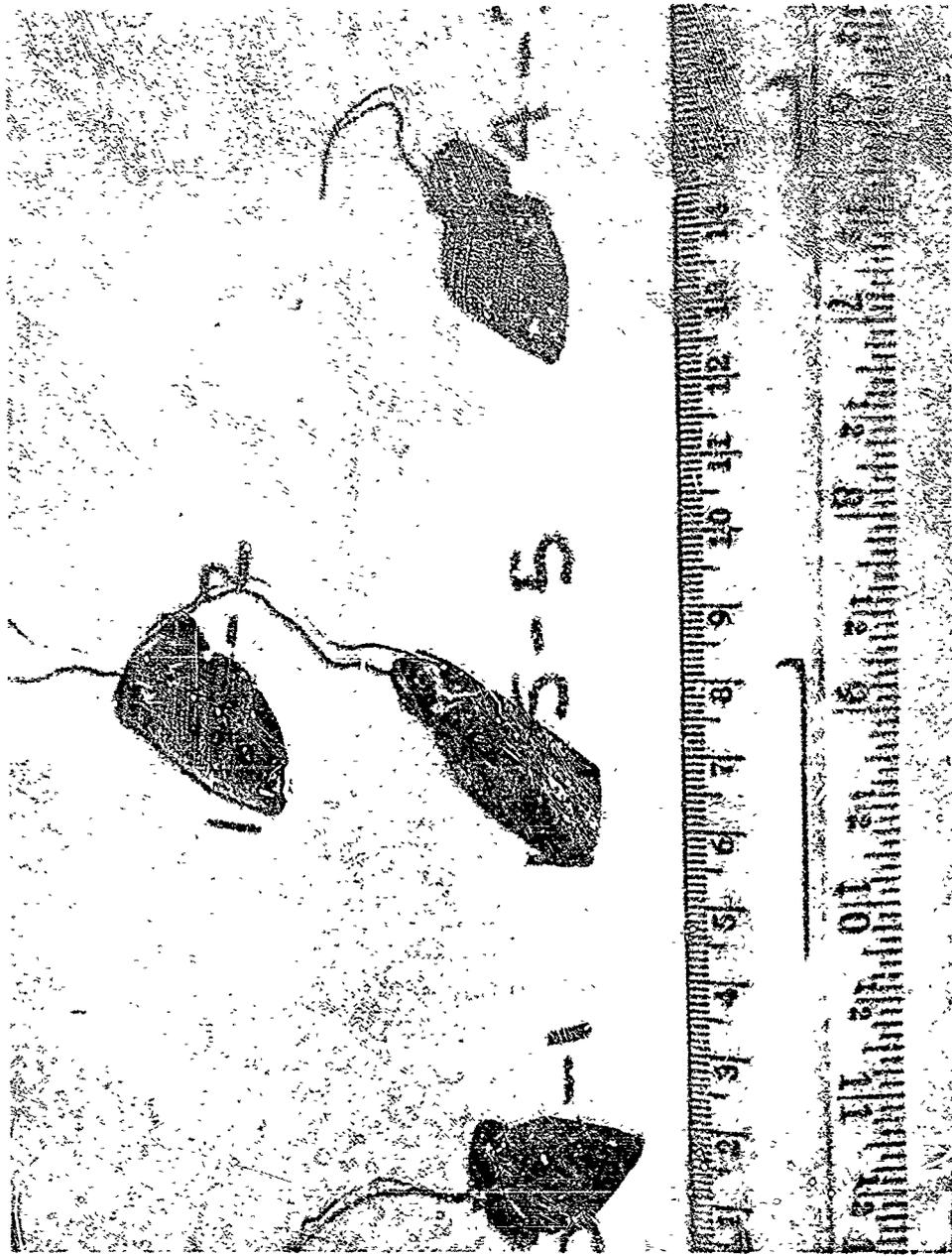
Figure 29 - High Quality Ruby Crystals
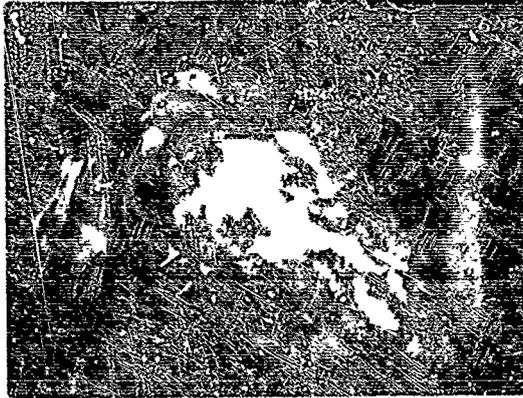
Figure 30 - Veiled Crystal Under Crossed Nicols
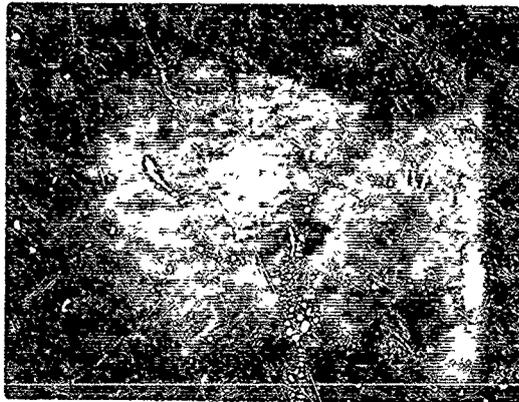
Figure 31 - High Quality Crystal Under Crossed Nicols
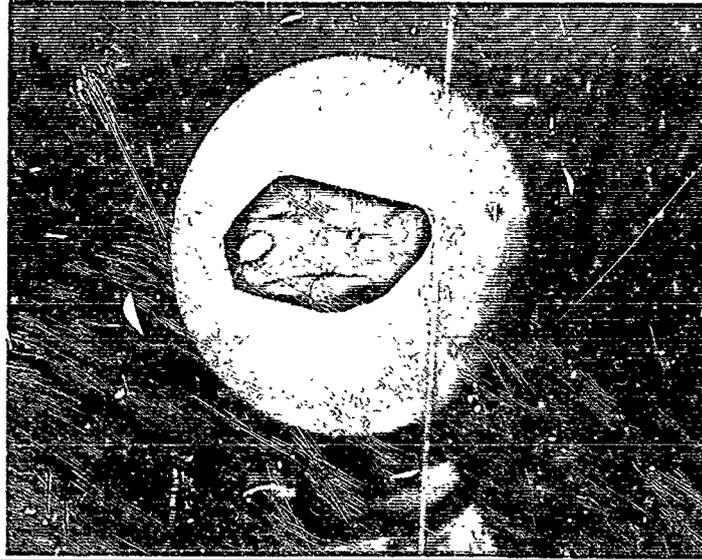
Figure 32 - High Quality Crystal by Transmitted Light

Figure 33 - High Quality Crystal Under Crossed Nicols

Crystal Quality and Testing (Continued)

cessfully to yield high quality crystals. Flame fusion materials whether boule or disc when used as seeds have always yielded much lower quality crystals.

4.5 Laser Rods and Laser Testing

The larger crystals grown under conditions given in Section 3.2.7 were examined microscopically for veil free and defect free areas. The crystals were then cut with a diamond wheel so as to remove the defective material and the molten salt seed. The rough rods were cut perpendicular to the axis and centerless ground to form cylindrical laser rods. Several rods in various stages of preparation are shown in Figure 34. Nearly confocal ends were then ground, polished and finally silver coated to 100 percent and 98 percent reflecting. The confocal radii were 1.5 times the rod length except as noted in Table III for rods No. 3 and 7.

All the ruby rods were lased at liquid nitrogen temperature ($77^\circ K$). The data are summarized in Table III.

The ruby rod and an EGG FX-42 flashtube were placed parallel and in fairly close proximity to each other along the line foci of an elliptical cavity (actually, nearly circular) having Alzac reflecting walls. The ruby was held in position inside a clear glass dewar containing the liquid nitrogen by means of a small rubber O-ring at the tip of a brass tube through which the radiation could exit to the photodetector. The latter was the TRG type 105 built around the ITT F4000(SI) photodiode which has very high frequency response and linearity over a wide dynamic range. The unit was generally used with an opal diffusing plate placed in front of the phototube, the combination having been calibrated by TRG at $6943^\circ A$ in volts/megawatt using Q-switched pulses. The attenuation factor of the diffusing plate was separately measured at Airtron, in case weak signals required its removal. The output of the photodetector was applied to one beam of a Tektronix dual-beam oscilloscope, and a signal proportional to the flashlamp light output was simultaneously applied to the other beam.

Lasing could thus be seen as a sharp discontinuous rise in the output of the laser photodetector occurring at some considerable time after the onset of the flashlamp pulse (generally, past its peak). (Figure 35). The absence of a laser pulse on the scope below a certain value of flashlamp energy and/or with the light path to the detector blocked, prove its origin to be laser oscillation in the crystal. The high frequency response of the TRG photodetector yields a fairly faithful reproduction of the laser pulse on the scope. (Thus, the spiking output of a ruby rod supplied by Adolph Meller & Co. is easily seen.) (Figure 36). The instantaneous power of the laser output is then determined from the deflection on the scope, and the total energy of the pulse is obtained by graphically integrating the power over the time duration of the pulse. The relatively small amplitude of spiking of the Airtron ruby rods made this calculation easy.

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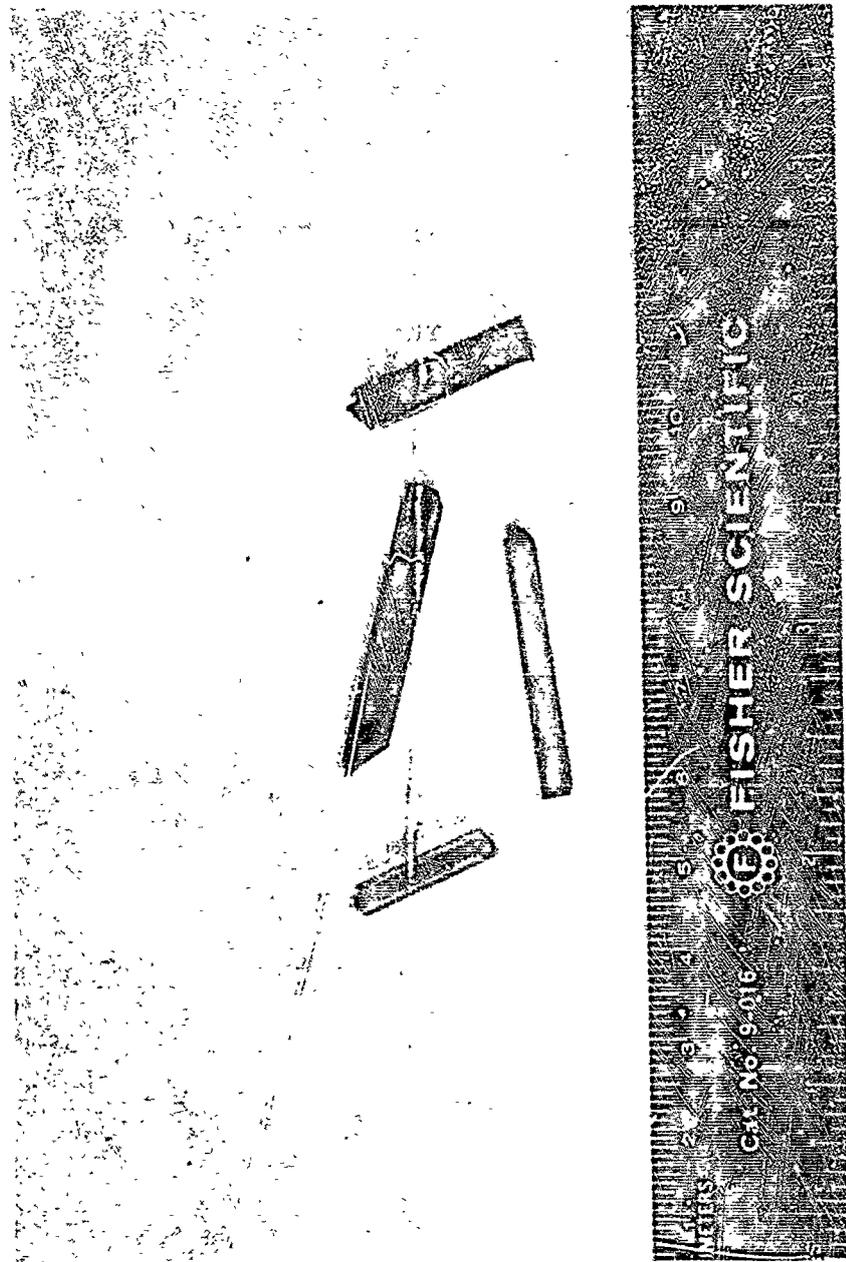
Figure 34 · Hydrothermal Rods

TABLE III

RESULTS OF LASER ROD TESTS

Rod No.	Length (mm)	Diameter (mm)	Energy Out (joules)	for	Energy In (joules)	Duration of Laser Pulse (μsec.)	Threshold (joules)
1	14	2.2	----------		---	---	<750
2	16	3.2	----------		---	---	600
3*	25.4	3.2	4.5×10^{-4}		625	300	360
4	12	3	0.4×10^{-4}		500	220	440
5	19	3.2	5×10^{-4}		625	280	<400
6	12.5	3.2	1.3×0^{-4}		650	370	440
7**	25.4	3.2	4×10^{-4}		400	130	<320

* Confocal radius 3/4 of the rod length.

** Meller flame fusion ruby laser rod. Parallel ends.

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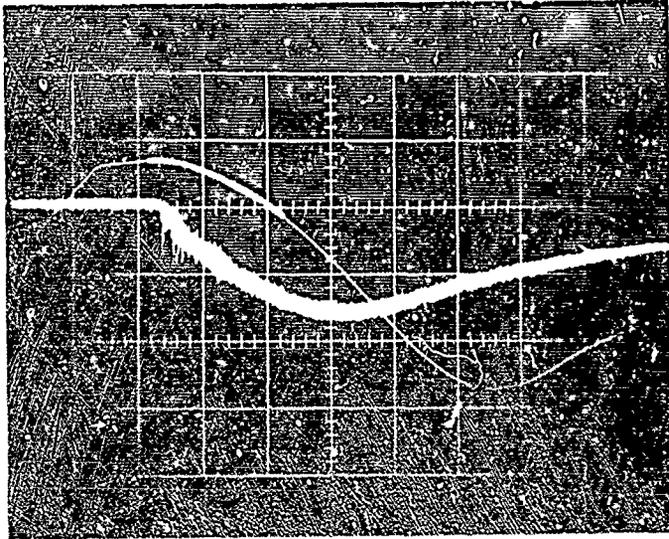
Figure 35 - Trace of Hydrothermal Ruby Laser Crystal
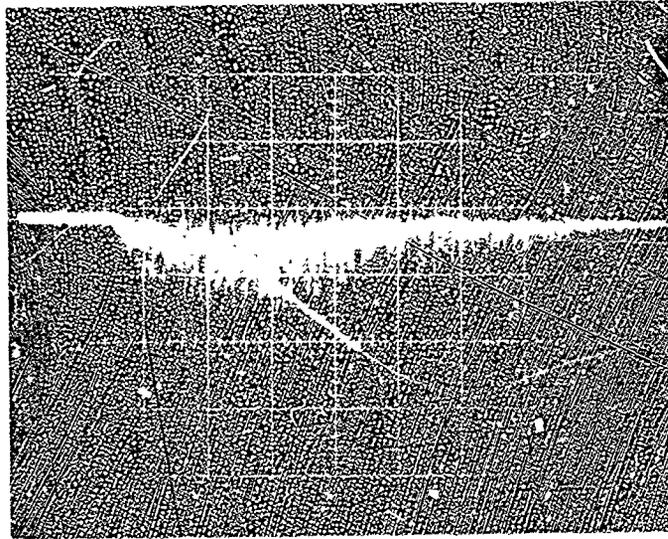
Figure 36 - Trace of Flame Fusion Ruby Laser Crystal

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Crystal Quality and Testing (Continued)

The value of "threshold" for lasing were taken as the minimum values of electrical energy $(1/2 \ CV^2)$ stored up in the flashlamp capacitor bank for which a laser pulse could be obtained. These values will be very much a function of the output pulse shape of the flashlamp with its power supply, the efficiency and spectral characteristics of the flashlamp, and the efficiency of the laser head as well as of the properties of the crystal rod. The flashlamp output had about 70 to 75 percent of its energy in an approximately half sine wave pulse of about 0.8 milliseconds duration with the remaining energy in a succeeding pulse of similar shape and duration. The lasing pulses tabulated here occurred during the main flashlamp pulse. All input energies given, though, are of the total electrical energy input to the flashlamp.

The outputs of the hydrothermal ruby rods appear to be low. However, a 1.25 inch long x 0.2 inch diameter Verneuil grown ruby from Adolph Meller Co. yielded a similar level of output. The light output of the ruby rods did, generally, traverse a small thickness of liquid nitrogen (no more than 1/4") and could, possibly, have been partly intercepted by the brass output tube before reaching the photodetector. These, or other possible mechanisms reducing the measured light output, are being looked into.

The ruby rods from Meller showed the usual strong spiking in its laser output. The hydrothermally grown rods, however, showed very little spiking; i.e., generally, less than 10 percent of the laser pulse amplitude. Spiking is now known to be affected by the geometry of the laser resonant cavity. The Meller rod had plane-parallel ends; whereas, the Airtron rods were off-confocal with the radius of curvature of each end set at 1.5 times the rod length (except for Airtron's No. 3, where the factor was 0.75). All rods were silvered to 100 percent reflectivity at one end and to 99 percent at the other end, in the case of the Airtron rods, and to 98 percent to 95 percent in the case of the Meller rod. The effect of geometry on spiking has not yet been studied by us sufficiently to know whether or not the differences in spiking behavior are mainly a consequence of the differences in method of ruby growth.

R. Pressley of the David Sarnoff Research Center, R. C. A., Princeton Laboratories, confirmed the observed laser action for rods Nos. 1 and 2. The R. C. A. head contained a G. E. 524 spiral flashlamp into which the rod was inserted for flashing. With this arrangement, thresholds of 1,000 and 1,100 joules for rods Nos. 1 and 2, respectively, were obtained which are slightly higher than those in the Airtron laser head.

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5.0 CONCLUSIONS

A program has been carried out to develop the manufacturing process, techniques and equipment for the hydrothermal preparation of large, good quality ruby crystals. The success of the program can be measured by the achievements not only of growing crystals suitable for laser rod fabrication but also by the contributions to autoclave technology and to the science of hydrothermal crystal growth.

A technique was developed for autoclave seal preparation for attaining high temperature-high pressure sealing of these vessels. In order to do this, special seal lapping and seal polishing tools were designed. An anvil type wrench was developed to be used on the main nut in opening the autoclaves and an extractor was constructed to remove swelled silver cans from the autoclave after a run. The need for such an extractor arose when the large can technique was introduced into the process.

This technique greatly facilitated crystal growth development work by assuring greater success in achieving pressure balance during each run. As a result of the pressure balance, fewer silver can and autoclave leaks were experienced.

The solubility of Al_2O_3 and K_2CO_3 was determined as functions of temperature, pressure, and mineralizer concentration. These data served as a background guide for the growth of ruby crystals in the large autoclaves

In the development of this crystal growth process to produce large, high quality crystals, the growth rate data were gathered and compiled for pressure, temperature, and mineralizer variations. The process was developed to that point where large ruby crystals (20 - 90 grams) could be grown in Waspalloy autoclaves within very reasonable times. The quality of the crystals was such that rods 10 to 25 mm long and 2 - 3 mm in diameter could be fabricated and lased at liquid nitrogen temperatures. Furthermore, t e strain contained in the hydrothermal crystals was very low compared to flame fusion materials.

The crystal growth results, particularly the quality of the crystals as reflected by the lasing and lack of strain coupled with the hydrothermal crystal growth technology involved under this Contract, are sufficiently encouraging to indicate that the method of hydrothermal crystal growth can be applied to ruby for the economic production of large, high quality crystals.

6.0 RECOMMENDATIONS FOR FUTURE WORK

Future work on the hydrothermal process for the manufacture of ruby should be directed primarily at scaling-up the process to produce larger crystals and to modify growth conditions to improve crystal quality. Specific problems which must be solved in order to carry out these objectives are as follows:

1. A sintered, fused or other forms of nutrient prepared by a very economical process must be found so that the nutrient price will be nearly that of the raw material's cost. The second requirement of the process is that it be capable of yielding quantities of materials.

2. The growth parameters and/or equipment and controls must be modified to obtain maximum possible quality. The two most important flaws to be eliminated or minimized are banding and veiling.

3. Seed source, orientation and preparation must be investigated to produce the highest quality crystal to commensurate with rates and costs. Of specific note, it would be most desirable to establish a technique for the reuse of seeds.

4. The general problems attendant to the scaling-up of such a process must be solved to produce crystals of highest quality and lowest cost. The immediate objectives of the scale-up should be to produce crystals capable of yielding laser rods of the size and quality which will satisfy current ruby laser needs. At present, the requirements are for laser rods 2 to 3 inches long by 1/4 inch in diameter.

5. The scale-up should involve examination of the autoclave situation in view of the construction materials, seal designs, and cost. While the Waspalloy appears to be a satisfactory construction material, the high cost and availability of large size ingots warrant attempts to use other materials. The design of the autoclave seal is one other area worthy of investigation in order to improve the sealing reliability factor.

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8.0 <u>APPENDICES</u>

   8.1 <u>APPENDIX I</u> - SAPPHIRE AND RUBY SOLUBILITY DATA IN TEM-PRES

TABLE IV

Sample	Molality	Temperature ($^{\circ}$C)	$P \times 10^3$	Percent Solubility
1	2	430	10	3.2
2	2	475	10	3.9
3	2	525	10	4.5
4	2	575	10	5.4
5	3	425	10	4.5
6	3	442	10	4.4
7	3	466	10	5.5
3	3	485	10	5.8
9	3	522	10	5.2
10	3	542	10	6.6
11	3	433	20	4.6
12	3	446	20	4.5
13	3	473	20	5.4
14	3	492	20	5.8
15	3	526	20	6.5
16	3	546	20	6.7
17	3	566	20	6.7
18	3	590	20	7.3
19	3	433	30	4.4
20	3	447	30	4 5
21	3	471	30	4.9
22	3	492	30	5.6
23	3	526	30	5.9

TABLE IV (Continued)

Sample	Molality	Temperature (°C)	$P \times 10^3$	Percent Solubility
24	3	543	30	6.6
25	3	567	30	6.5
26	3	585	30	7.5
27	4	429	5	4.9
28	4	455	5	5.0
29	4	481	5	6.3
30	4	503	5	6.5
31	4	429	10	5.2
32	4	449	10	5.3
33	4	450	10	4.4
34	4	450	10	4.3
35	4	471	10	6.2
36	4	492	10	6.8
37	4	520	10	5.9
38	4	530	10	7.7
39	4	548	10	6.1
40	4	555	10	6.5
41	4	555	10	7.1
42	4	570	10	8.8
43	4	429	20	4.5
44	4	452	20	5.5
45	4	470	20	6.0
46	4	492	20	6.6

TABLE IV (Continued)

Sample	Molality	Temperature (°C)	P x 10³	Percent Solubility
47	4	528	20	7.2
48	4	550	20	7.7
49	4	564	20	8.1
50	4	585	20	8.7
51	4	428	30	3.7
52	4	457	30	4.3
53	4	473	30	5.4
54	4	493	30	6.1
55	4	531	30	7.0
56	4	552	30	6.3
57	4	562	30	7.9
58	4	584	30	6.4
59	5	420	5	5.4
60	5	425	5	5.6
61	5	442	5	5.4
62	5	468	5	6.5
63	5	463	5	6.3
64	5	465	5	6.5
65	5	509	5	6.8
66	5	512	5	7.2
67	5	534	5	7.1
68	5	450	10	5.8
69	5	450	10	5.4

TABLE IV (Continued)

Sample	Molality	Temperature (°C)	P x 10^3	Percent Solubility
70	5	450	10	6.1
71	5	485	10	6.8
72	5	520	10	7.8
73	5	555	10	7.1
74	5	445	20	5.1
75	5	445	20	5.5
76	5	482	20	7.1
77	5	520	20	6.9
78	5	520	20	7.5
79	5	525	20	8.5
80	5	550	20	7.9
81	5	550	20	8.3
82	5	560	20	8.5
83	5	442	30	4.9
84	5	442	30	5.0
85	5	469	30	5.9
86	5	475	30	5.7
87	5	525	30	7.2
88	5	536	30	7.8
89	5	565	30	8.2
90	5	569	30	8.3
91	7	420	10	5.6
92	7	452	10	6.2

TABLE IV (Continued)

Sample	Molality	Temperature ($^{\circ}$C)	$P \times 10^3$	Percent Solubility
93	7	465	10	6.8
94	7	501	10	8 3
95	7	505	10	7.9
96	7	522	10	8.7
97	7	551	10	9.8
98	7	428	20	5.2
99	7	449	20	5.7
100	7	466	20	6.6
101	7	486	20	7.2
102	7	538	20	8.9
103	7	559	20	9.1
104	4	425	5	4 5
105	4	500	5	6.5
106	4	575	5	8.5
107	7	430	5	5.3
108	7	495	5	7.5
109	7	550	5	8.0
110	4	425	30	3.6
111	4	505	30	6.2
112	4	570	30	8.0
113	7	430	30	4.9
114	7	505	30	6.6
115	7	580	30	8.5

TABLE IV (Continued)

Sample	Molality	Temperature ($^{\circ}$C)	P x 10^3	Percent Solubility
116	5	425	10	2.9
117	5	455	10	3.2
118	5	490	10	3.9
120	5	552	10	5.5
121	5	575	10	6.1
122	4	425	10	2.4
123	4	460	10	2.7
124	4	505	10	3.0
125	4	530	10	3.4
126	4	550	10	3.9
127	4	580	10	5.3
128	4	425	10	5.2
129	4	475	10	6.2
130	4	500	10	6.8
131	4	525	10	7.7
132	4	550	10	8.1
133	4	575	10	8.5
134	5	430	10	5.1
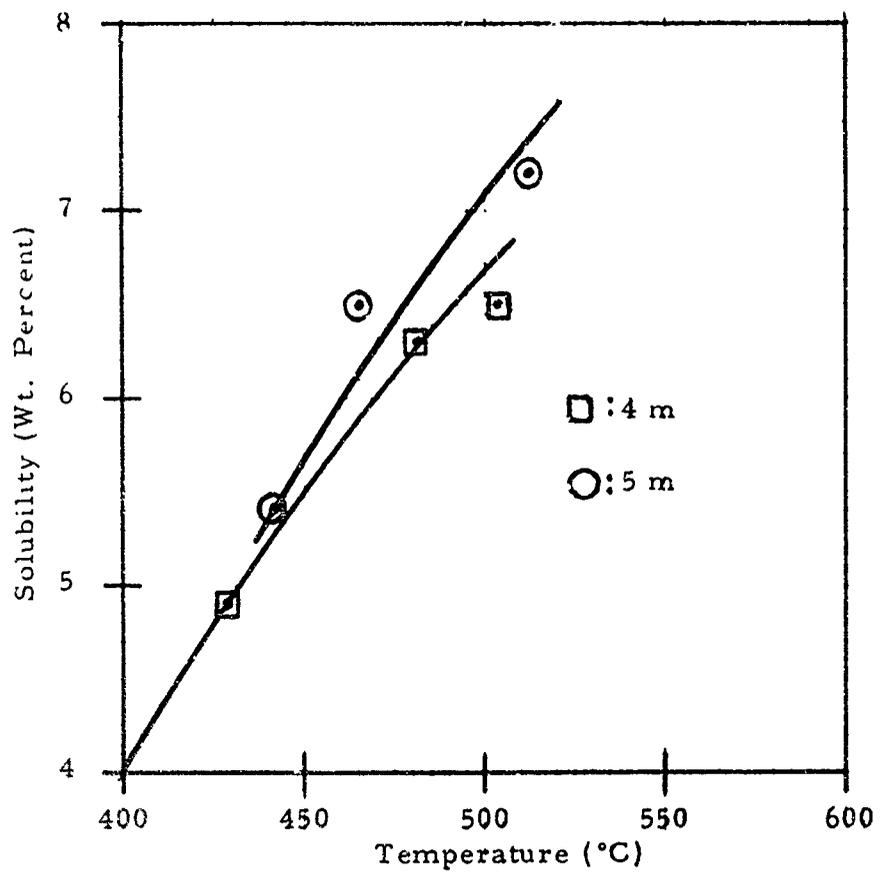
Figure 37 - Solubility vs. Temperature at 5,000 psi
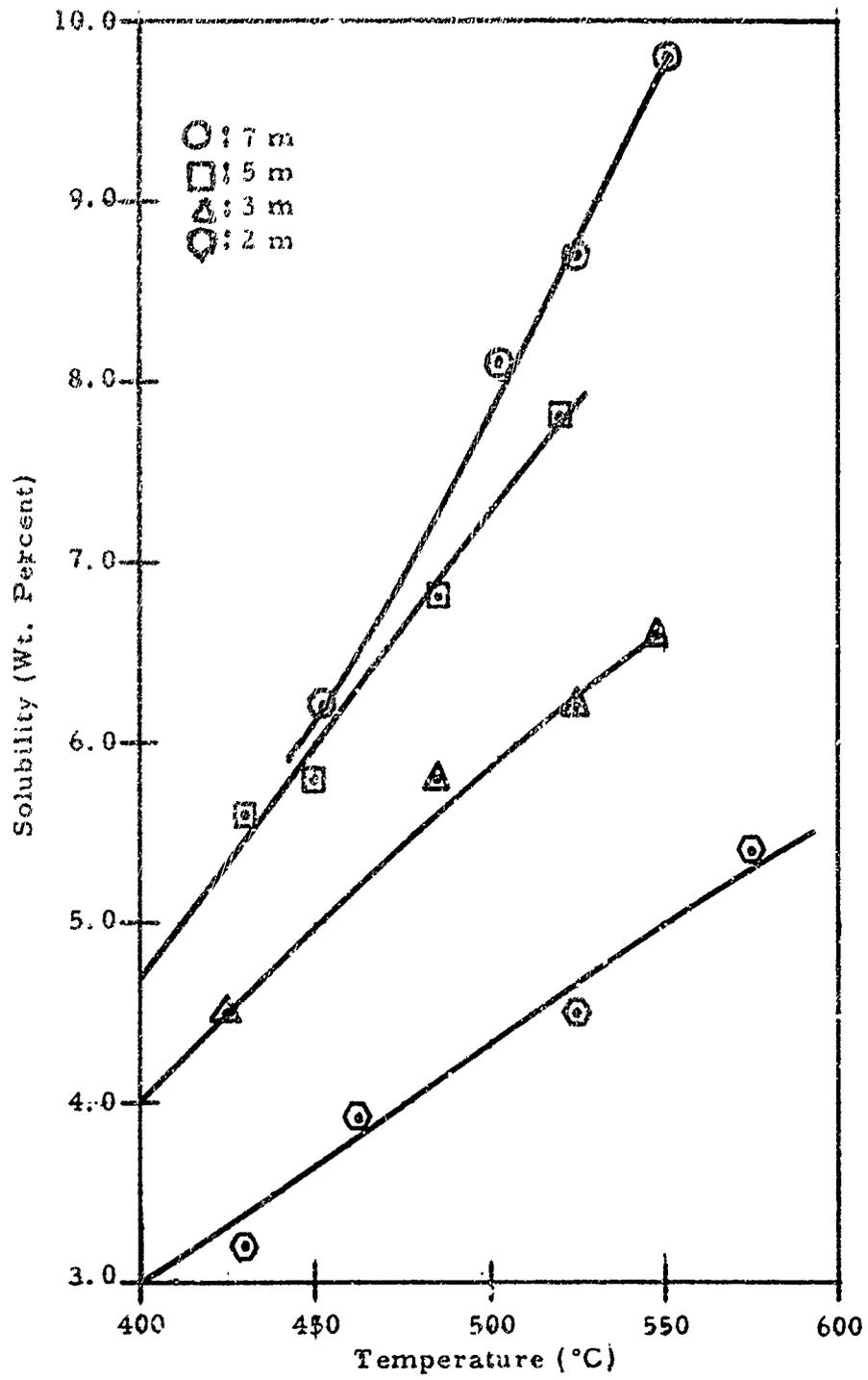
Figure 38 · Solubility vs Temperature at 10,000 psi

- 71 -
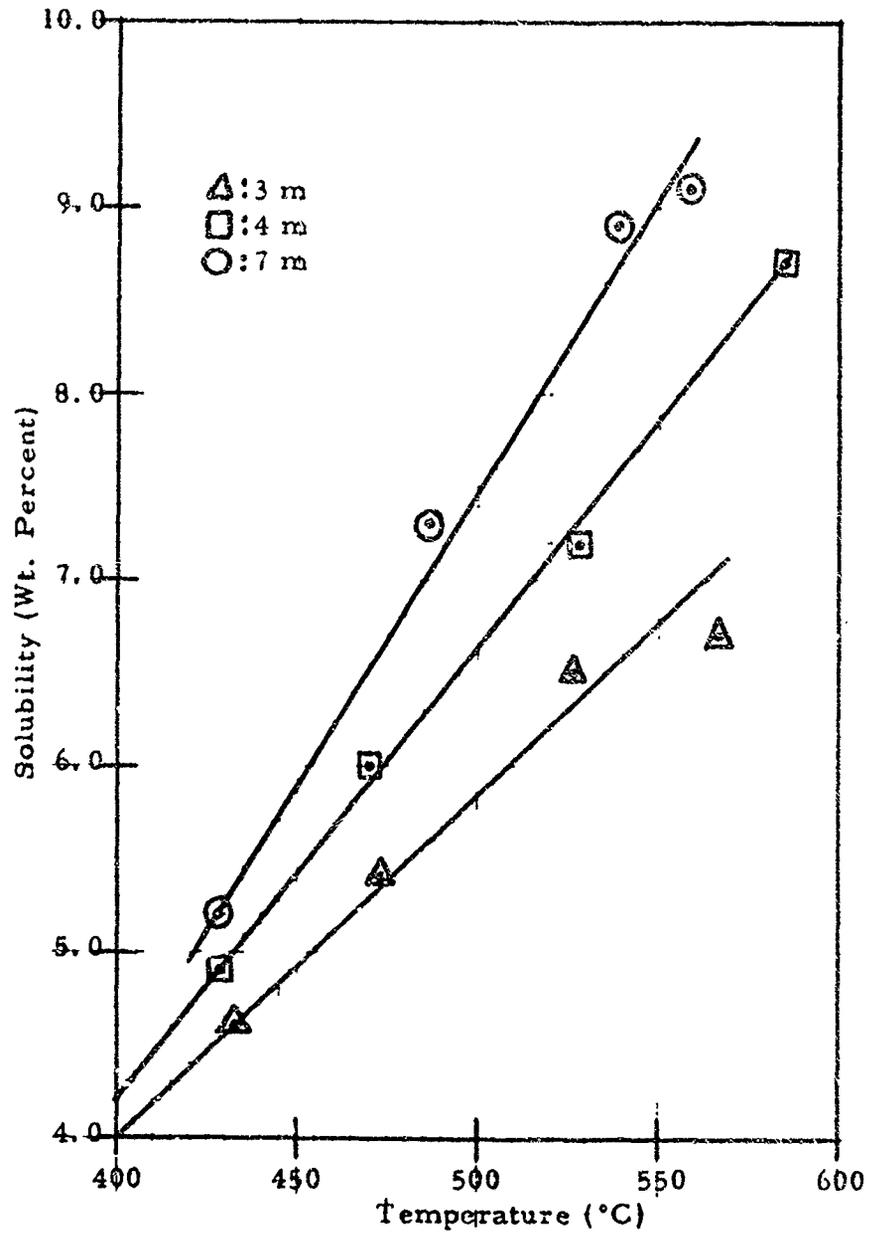
Figure 39 - Solubility vs. Temperature at 20,000 psi
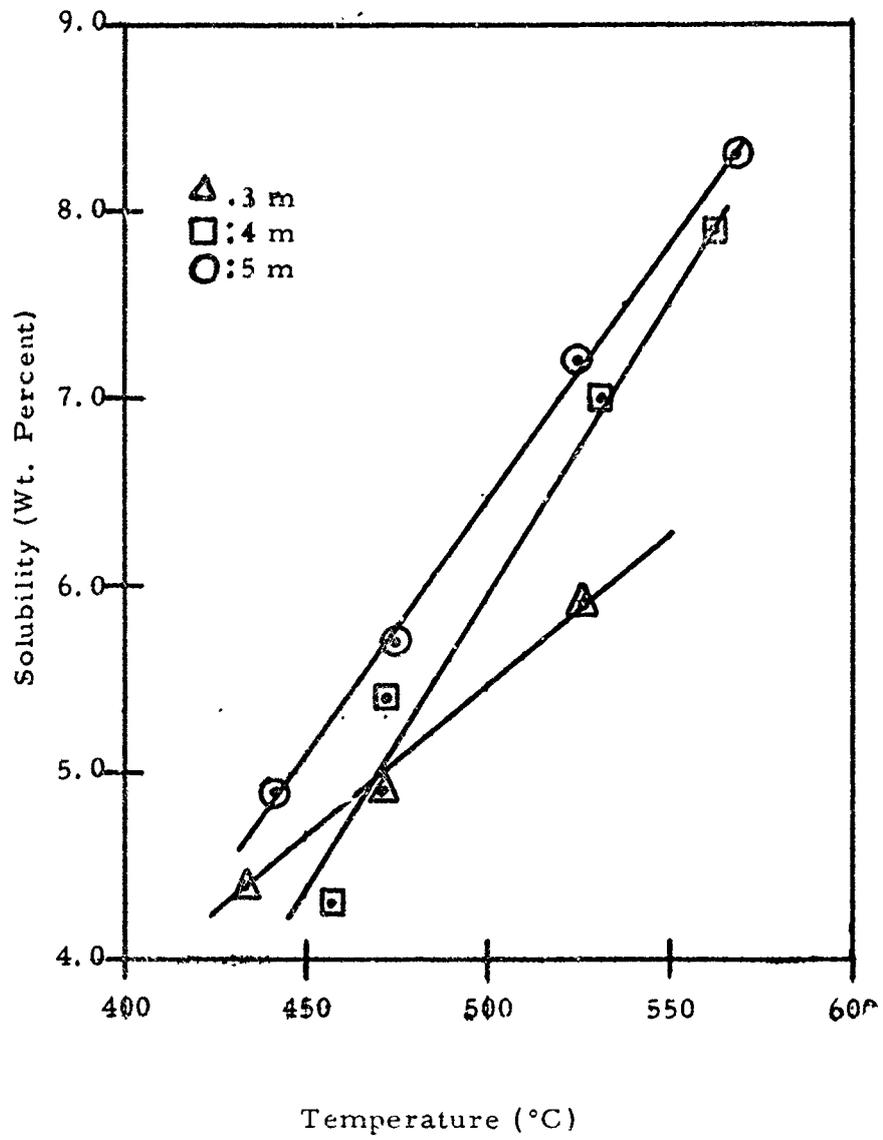
Figure 40 - Solubility vs. Temperature at 30,000 psi
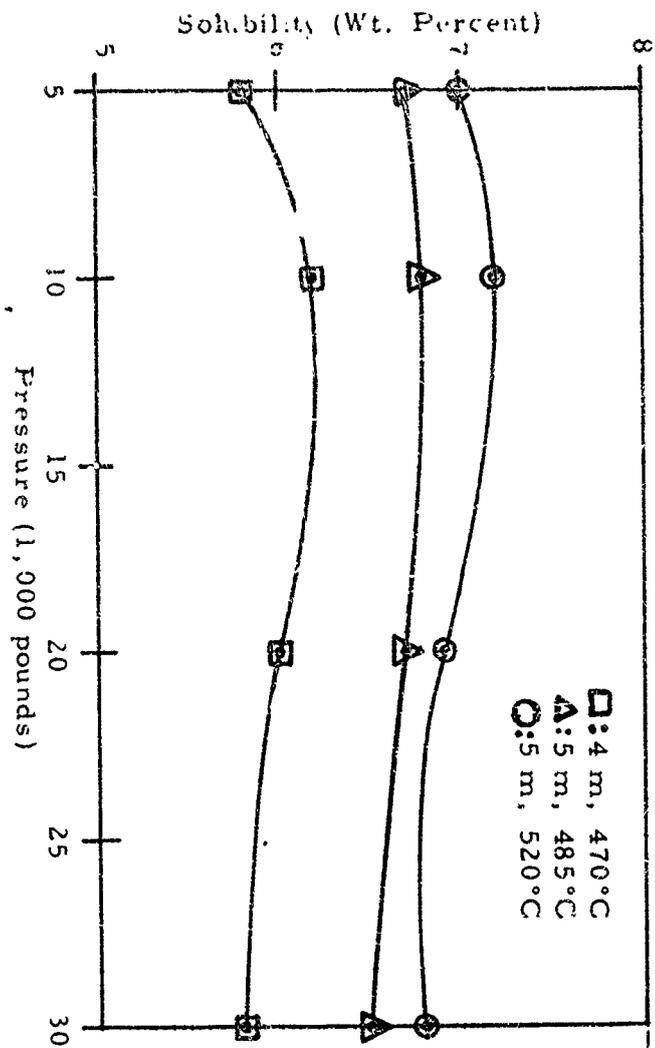
Figure 41 – Solubility vs. Pressure
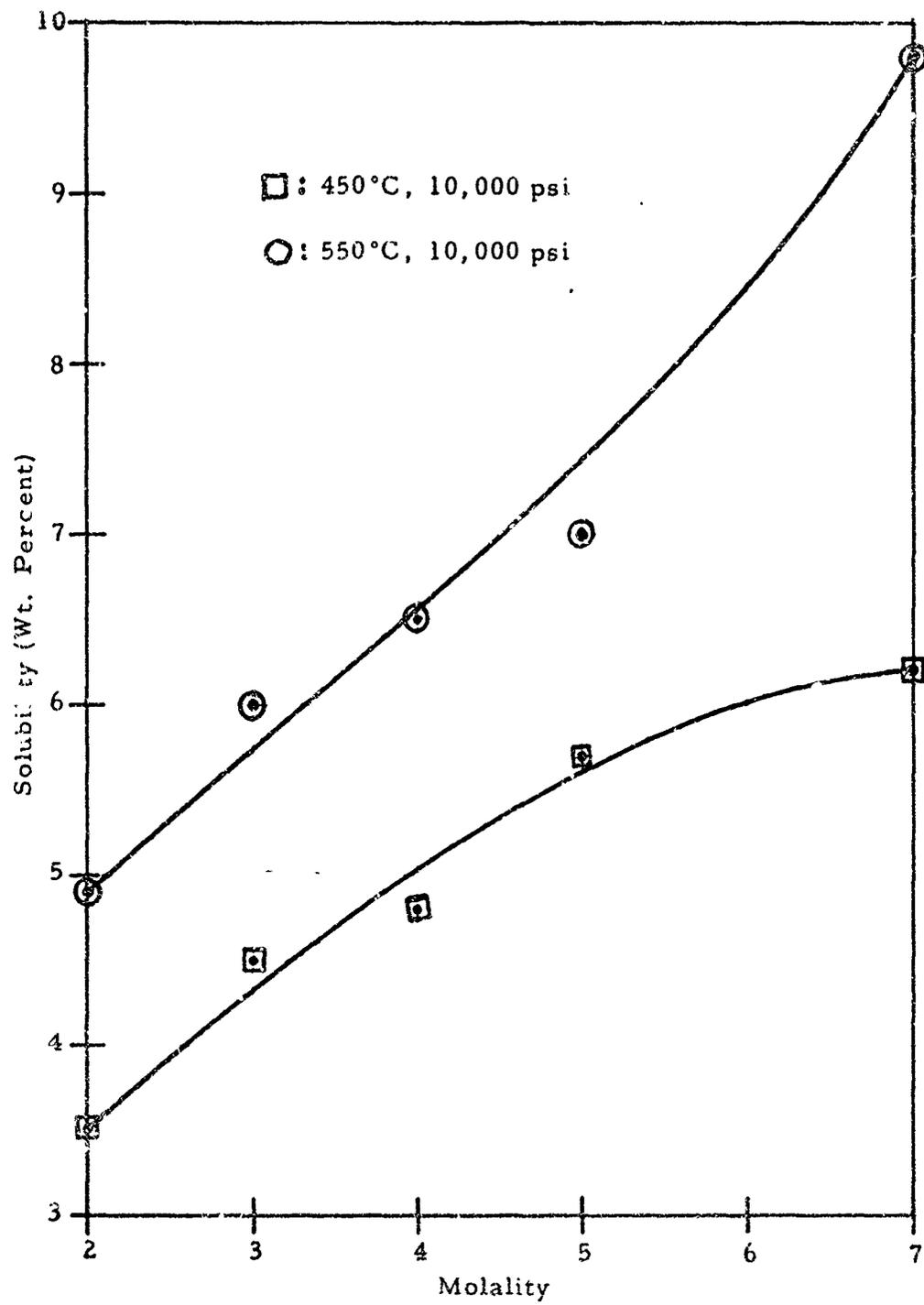
Figure 42 - Solubility vs. Mineralizer Concentration

Appendices (continued)

6.2 APPENDIX II - TEM-PRES CRYSTAL GROWTH DATA

TABLE V

Nutrient	Solvent	Dopant	Seed	Solution T (°C)	ΔT (°C)	$P \times 10^3$	Growth Rate in./day	Comments
Sapphire	3 m K_2CO_3	------	Sapphire Rod	515	75	10	0.025	Excellent quality, no flaws visible under microscope or crossed polaroids.
Sapphire	4 m K_2CO_3	------	Sapphire Rod	520	75	10	0.030	Excellent quality, no flaws visible under microscope or crossed polaroids.
Sapphire	5 m K_2CO_3	------	Sapphire Rod	525	75	10	0.040	Excellent quality, no flaws visible under microscope or crossed polaroids.
Sapphire	5 m K_2CO_3	------	Sapphire Rod	520	80	10	0.050	Cracked and flawed.
Sapphire	7 m K_2CO_3	------	Sapphire Rod	510	70	10	0.020	Excellent quality.
Sapphire	5 m K_2CO_3	------	Sapphire Rod	520	80	10	0.039	Excellent quality.
Sapphire	5 m K_2CO_3	K_2CrO_4	Sapphire Rod	520	75	10	0.010	Cracked non-uniform doping, very dark.
Sapphire	5 m K_2CO_3	K_2CrO_4	Sapphire Rod	530	85	10	0.015	Cracked non-uniform doping, very dark.
Ruby	5 m K_2CO_3	K_2CrO_4	Sapphire Rod	520	80	10	0.010	Cracked non-uniform doping, very dark.

TABLE V (Continued)

Nutrient	Solvent	Dopant	Seed	Solution T (°C)	ΔT (°C)	P x 10^3	Growth Rate in./day	Comments
Ruby	5 m K_2CO_3	------	Sapphire Rod	510	70	10	0.040	Uniform doping but cracked and flawed.
Ruby	5 m K_2CO_3	------	Sapphire Rod	500	70	10	0.036	Uniform doping but cracked and flawed.
Ruby	4 m K_2CO_3	------	Sapphire Rod	520	80	10	0.035	Uniform doping but cracked and flawed.
Ruby	4 m K_2CO_3	------	Molten Salt Ruby Crystal	520	80	10	Not determined	Excellent quality.

Appendices (continued)

8.3 APPENDIX III - HYDROTHERMAL CRYSTAL GROWTH RUNS

TABLE V: A

Run	Warm-up Time (hrs)	Solvent	Nutrient	Seeds	Bottom Temp (°C)	Top Temp (°C)	ΔT (°C)	Pressure	Results
49	24	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion ruby	500	395	105	10,000	Seeds dissolved.
50	48	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion ruby	490	420	70	9,500	Seeds dissolved.
51	48	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion ruby	520	435	85	10,400	Seeds dissolved.
52	72	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion & molten salt	525	450	75	10,000	Seeds etched, some faces appear to have growth.
53	96	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion & molten salt	494	427	67	10,000	Growth faces, no weight change.
54	96	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion & molten salt	515	448	67	9,500	Growth faces, loss in weight.
55	96	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion & molten salt	525	415	110	11,000	Growth faces, slight weight increase.
56	96	4 m K_2CO_2	Flame fusion ruby scrap	Flame fusion ruby	520	440	80	8,400	Low rate, high Cr concentration.
57	96	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion ruby	531	281	250	Seal leaked	--------
58	96	4 m K_2CO_3	Flame fusion ruby scrap	Flame fusion ruby	516	366	150	9,000	Definite growth, all seeds increased in weight.

TABLE VI B

Run No.	Internal Fill (%)	External Fill (%)	Baffle Area (%) & Style	Warm-up Time (hrs)	Growth Period (days)	Bottom Temp (°C)	Middle Temp (°C)	Top Temp. (°C)	ΔT (°C)	Pressure (psi)	Comments
59	71	43	20 old	96	19	540	444	382	158	7,000	Can leaked, no growth.
60	72	43	10 old	96	3	549	470	426	123	10,000	Small seeds dissolved, slight growth of nutrient.
61	71	44	10 old	96	20	540	470	430	110	10,000	Growth on seeds & nutrient, flawed, cloudy, uniform.
62	71	44	10 old	48	7	540	465	361	179	10,000	0.5% Cr doped nutrient material.
63	71	44	10 old	48	18	525	500	485	40	11,100	Slight growth on seeds. Growth of nutrient, clear, uniform.

Large silver cans (1.44 inch diameter) used for all runs and 4 m K_2CO_3 solutions were used as solvent.

TABLE VI C

Run No.	Internal Fill (%)	External Fill (%)	Baffle Area (%)	Growth Period (days)	Bottom Temp (°C)	Middle Temp (°C)	Top Temp (°C)	ΔT (°C)	Pressure (psi)	Maximum Growth Rate (mils/day)	K_2CO_3 Conc. (m)	Purpose of Run Comments, Etc.
64	72	43	20	9	520	520	490	35	11,000	0	4	No growth.
65	72	43	No	7	525	575	440	85	10,000	6	4	To see effect of no baffle.
66	54	44	10	7	520	485	440	80	9,300	32	1.5	Study rate vs. m of K_2CO_3. Can leaked.
67	72	43	No	7	530	445	410	120	9,400	20	4	Same as No. 65 but with increased ΔT.
68	54	44	10	7	525	490	445	80	11,000	21	1.5	Repeat No. 66.
69	61	44	10	8	520	470	440	80	9,500	7	2.5	Same as No. 66.
70	51	44	10	7	525	490	445	80	10,100	12	1.0	Same as No. 66, can leaked.
71	47.5	44	10	7	535	480	455	80	10,000	27	0.5	"
72	50	44	10	0	---	---	---	--	-------	--	0.5	Autoclave seal leaked.
73	57.5	44	10	1	---	---	---	--	-------	--	2.0	Can leaked, autoclave seal leaked.
74	50	44	10	7	527	470	443	84	9,700	35	1.0	Repeat No. 70, can leaked.

TABLE VI C (Continued)

Run No.	Internal Fill (%)	External Fill (%)	Baffle Area (%)	Growth Period (days)	Bottom Temp (°C)	Middle Temp (°C)	Top Temp. (°C)	ΔT (°C)	Pressure (psi)	Maximum Growth Rate (mils/day)	K_2CO_3 Conc. (m)	Purpose of Run Comments, Etc.
75	81	68	10	1	---	---	---	--	------	--	1.5	Study effect of pressure, autoclave leaked.
76	69	58	10	3	525	500	465	60	17,500	197	1.5	Same as No. 75.
77	81	68	10	3	495	460	430	65	31,000	263	1.5	Same as No. 75.

TABLE VI D

Run No.	Internal Fill (%)	Bottom Temp (°C)	Avg Top Temp (°C)	ΔT (°C)	Avg Temp. (°C)	Pressure (psi) (10^3)	Conc. K_2CO_3 (m)	Growth Period (days)	Growth Rates and Comments	Operations and Observations
78	71.5	504	452	52	469	13.0	1.5	5	3 inch can	Heavy SN–slight leak in weld
79	71.5	521	493	28	502	19.7	1.5	8	61 mils/day-60° rod, Rung No. 1	SN, very slight AgA
80	75.0	529	507	22	514	21.3	2.0	5	109 mils/day-60° rod, Rung No. 1	SN, very slight AgA
81	77.0	500	452	48	468	19.0	2.5	4	86 mils/day-60° rod, Rung No. 1	------
82	79.5	520	504	16	512	15.0	3.0	1	225 mils/day-60° rod, Rung No. 1	Shut off because suspected leak
83	79.0	512	495	17	500	23.2	3.0	3	40 mils/day-C flux plate, Rung No. 1	Slight SN, no AgA
84	83.0	524	506	18	512	17.0	4.0	4	59 mils/day-C flux plate, Rung No. 1	------
85	86.0	526	502	24	510	23.0	6.0	4	56 mils/day-C flux plate, Rung No. 1	No AgA, SN
86	85.5	451	420	31	430	16.7	4.0	1	No growth, seeds used for No. 87	Shut off because suspected leak

TABLE VI D (Continued)

Run No.	Internal Fill (%)	Bottom Temp (°C)	Avg Top Temp (°C)	ΔT (°C)	Avg Temp (°C)	Pressure (psi) (10^3)	Conc. K_2CO_3 (m)	Growth Period (days)	Growth Rates and Comments	Operations and Observations
87	85.5	453	411	42	425	15.7	4.0	1	No growth, C flux plate, Rung No. 1	Leaked, shutdown first day
88	75.5	520	490	30	500	14.3	4.0	3	9 mils/day-C flux plate, Rung No. 2	Slight AgA, no SN, leaked
89	85.0	526	500	26	509	17.0	8.0	3	56 mils/day-C flux plate, Rung No. 1	Leaked, no SN
90	88.0	463	419	44	434	21.0	6.0	1	No growth, seeds used in Run No. 92	Shutdown because of leak
91	86.0	---	---	--	---	----	6.0	-	3 inch can	Autoclave failed during warm-up

SN - Spontaneous Nucleation

AgA - Silver Attack

TABLE VI E

Run No.	Internal Fill (%)	Bottom Temp (°C)	Avg Top Temp. (°C)	ΔT (°C)	Avg Temp. (°C)	Pressure (psi · 10³)	K_2CO_3 Conc. (m)	Growth Period (days)	Growth Rate $<c>$ (mils/day)	Comments
92	88.5	462	429	40	442	25.4	6	4	16	Seal leak, no can leak.
93	85.0	548	521	27	530	27.3	6	3	58	Seal leak, no can leak.
94	87.0	485	457	28	466	25.8	6	3	22	------
95	86.0	475	455	20	462	15.0	6	-	--	3" can, run stopped. Can leaked during warm-up.
96	85.0	554	540	14	544	22.1	6	1	68	Seal leaked during warm-up, no can leak.
97	87.0	526	514	12	518	26.0	6	-	--	"
98	85.0	543	522	21	529	29.1	6	3	56	------
99	87.0	514	493	21	500	31.6	6	3	23	------
100	86.0	437	365	72	389	13.0	6	-	--	3" can, seal leaked during warm-up.
101	85.0	542	521	21	528	25.3	6	3	59	------
102	*	490	472	18	478	28.0	*	1	--	Seal leaked, no can leak, no growth.

TABLE VI E (Continued)

Run No.	Internal Fill (%)	Bottom Temp (°C)	Avg Top Temp (°C)	ΔT (°C)	Avg Temp. (°C)	Pressure (psi · 10^3)	K_2CO_3 Conc. (m)	Growth Period (days)	Growth Rate $<c>$ (mils/day)	Comments
103	**	---	---	--	---	----	**	-	--	Fill too high to reach growth temperature and pressure.
104	85.0	533	526	7	531	24.0	6	2	38	Seal leak, slight can leak due to weld, VERY HIGH QUALITY.
105	85.0	539	511	28	530	22.7	6	2	41	Seal leak, no can leak, VERY HIGH QUALITY.
106	85.0	530	521	9	524	27.8	6	1	26	Seal leak, no can leak, VERY HIGH QUALITY.
107	**	503	497	6	499	22.5	**	1	--	------

* Mixed 3 m KOH and 3 m K_2CO_3 used as solvent.

** Na_2CO_3 used as solvent.

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13 ABSTRACT

The hydrothermal growth of ruby crystals has been taken from the point of feasibility to the point where techniques, process and equipment have been developed whereby large crystals have been grown from which laser rods were cut.

The development of this process involved a study of the solubility of Al_2O_3 in K_2CO_3 as a function of pressure (5,000 - 30,000 psi), temperature (400°C - 600°C) and mineralizer content (2 - 7 m). The solubility was determined by the sample weight loss technique in a hydrothermal research apparatus. It was found that the solubility of Al_2O_3, in the ranges studies, increased with increasing molality and temperature but that the solubility was essentially independent of pressure. Solubilities of 2 - 9 weight percent of Al_2O_3 were observed under the preceding conditions. Using these data as a guide, the parameters affecting growth rate were studied while carrying out investigations to improve quality. The growth rate increased as expected with temperature and solvent concentration but exhibit a very rapid increase with pressure at about 15,000 psi. This was due to what appears to be a transition from a two-phase fluid below 15,000 psi to a single-phase fluid above this pressure.

Growth of high quality crystals was found to be dependent upon seed source, seed orientation and warm-up procedure. It was found that the highest quality growth was obtained when molten salt plates were used as seeds. These plates have [0001] faces as major faces for crystal growth. The warm-up of a vessel was found to be critical and a cycle was evolved which had a rapid warm-up to avoid complete dissolution of the seeds followed by a slow introduction to growth conditions. The conditions

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Item 13. Abstract – cont'd

established for the growth of good quality crystals at reasonable rate are as follows: 6m K_2CO_3 as solvent, 25,000 psi, crystallization temperature 525°C and nutrient temperature 530°C. The problem of banding appeared to be dependent on K_2CO_3 content of the solvent and the severity of this banding decreased as the K_2CO_3 molality increased. Veiling or cracking was reduced by using the molten salt seed plates and modified warm-up procedure.

From crystals grown by these procedures and with these conditions, several rods were fabricated into laser rods which, when pumped with a flashlamp, were caused to lase. This lasing action was about the same threshold and output as flame fusion ruby but was peculiar in that no spiking in the output was observed.